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Residual Oils	Hydrodenitrogenation	
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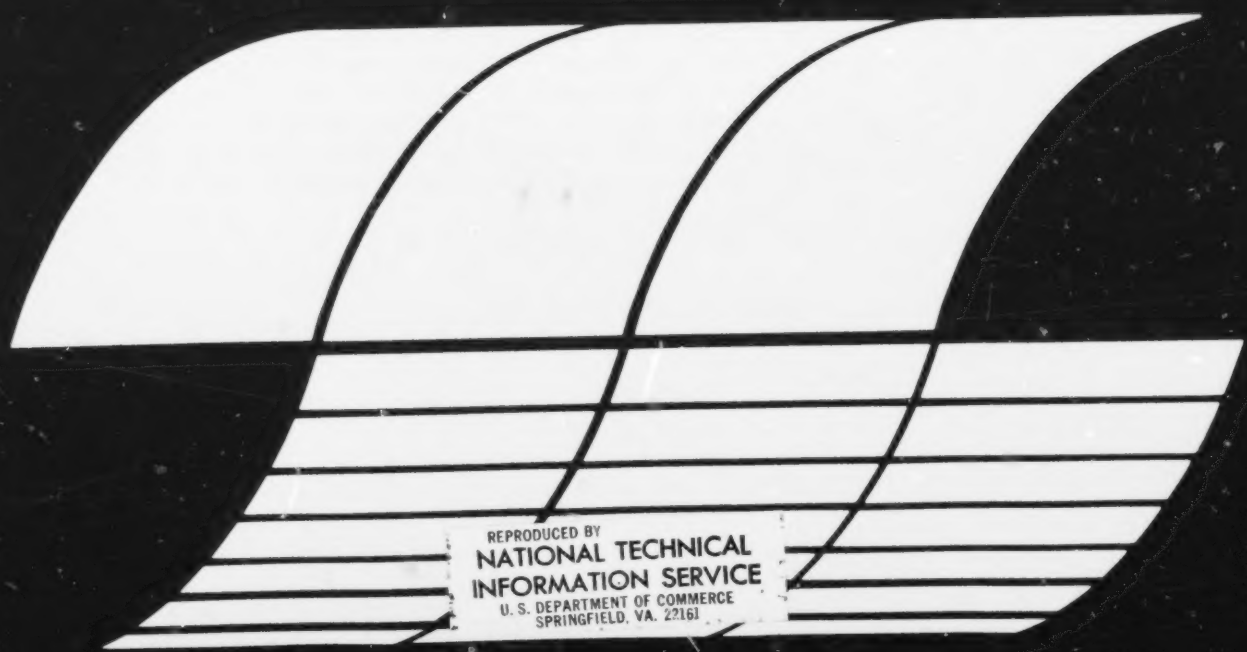

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ADVANCED OIL PROCESSING/UTILIZATION ENVIRONMENTAL ENGINEERING: EPA Program Status Report

by

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Abstract

This report is an annual status report of the IERL-RTP Advanced Oil Processing Program. The amounts and the normal practice and patterns of the usage of residual oil and contaminants in residual oil are projected, with the emission standards serving as a yardstick to indicate where potential problems exist. The development of both Environmental Assessment and Control Technology is given, and the alternatives, or choices of methods to use residual oil, are discussed. Methods available or considered for the use of residual oil include direct combustion, fluid bed combustion, partial oxidation, chemically active fluid bed (CAFB), direct hydrodesulfurization (HDS), and combinations of these technologies.

The history of the IERL-RTP program and the relationship of the CAFB to other alternatives are presented. The Environmental Assessment of residual oil usage and the control technology development efforts are outlined. The subobjectives, work tasks, and accomplishment plans, with funding levels, are presented. The participating contractors and grantees, with their scope of work outlines, and project descriptions are discussed. A section deals with the effort toward advanced HDS, hydrodenitrogenation (HDN), and demetallization techniques for residual oils and like-derived fuels. References and EPA reports and staff papers are listed in the appendices.

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1. SUMMARY

1.1 Executive Summary

The Industrial Environmental Research Laboratory, Research Triangle Park (IERL-RTP), North Carolina, is a part of the Office of Research and Development (ORD) within the Environmental Protection Agency (EPA). The IERL-RTP is responsible for managing programs to develop and demonstrate cost effective technologies to prevent, control, or abate pollution from operations with multimedia environmental impacts associated with the extraction, processing, conversion, and utilization of energy and mineral resources, as well as with industrial processing and manufacturing. The Laboratory also supports the identification and evaluation of environmental control alternatives of the program, consisting of in-house activities, contracts, grants, and interagency agreements, and contributes significantly to the protection of National health and welfare through the research and development of timely and cost-effective pollution control technologies.

Although EPA is primarily a regulatory agency, the vital supportive role of research and development activities within the overall EPA mission must not be overlooked. Adequate pollution control technology, for example, must be available before effective standards for the protection of public health and welfare can be set and successfully enforced; the development of ever more efficient and economical environmental control technology benefits not only the affected industry, but ultimately everyone. This is particularly true considering the present situation; in the long run, the protection of our environment and the conservation of our natural

resources are integral parts of meeting energy requirements in a viable manner. Advanced Oil Processing programs are concerned primarily with the area of energy resources utilization, especially the combustion and processing of residual oils, with secondary emphasis on applying new technologies to other fuels.

1.1.1 Mission of Standards Development/Implementation

It is one of the IERL-RTP stated objectives to establish a technical and economic research data base to support development of New Source Performance Standards (NSPS). Indeed, much of its research and development effort in fuel cleaning programs has been with the control of sulfur oxides as the basis for development/implementation of standards.

1.1.2 Program Areas (Subobjective/Work Plan Titles)

The Advanced Oil Processing program has three subobjectives, each with a number of project work areas:

A. Environmental Assessment--

Environmental Assessment of Residual Oil Usages

Analytical Support for Residual Oil Usage/Determination of Hazardous Substances

B. Chemically Active Fluid Bed Residual Oil Cleanup--

Chemically Active Fluid Bed Development and Support/Esso England

Chemically Active Fluid Bed Demonstration on Small Commercial Scale

Engineering Support of Chemically Active Fluid Bed Demonstration

Multiple Optional Service Contract Tasks in Support of the Fluid Bed Demonstration

C. Control Technology Development--

Hydrodesulfurization/Hydrodenitrification (HDS/HDN) Interactions in Liquid Fuels

Control Technology for HDS/HDN of Liquid Fuels

1.1.3 Funding Levels

Subobjective A (from Section 1.1.2) is funded at a level of $356,000.

Subobjective B (from Section 1.1.2) is funded at a level of $978,000.

Subobjective C (from Section 1.1.2) is funded at a level of $203,000.

1.2 Summary of Accomplishments

Accomplishments under the three subobjectives are:

° Advanced Oil Processing (Environmental Assessment)--Characterization of waste streams from oil processing methods and evaluation of the applicability of alternate advanced oil processing methods for utilization of petroleum residuals; evaluation of the application of available control technology; and publication of a manual of best available technology in coordination with the standards setting timetables. Significant accomplishments include:

°° Identification made of residual oil conversion/utilization as a national multimedia environmental problem with diverse potential consequences ranging from atmospheric sulfates to hazardous oil spills.

- Inventory completed of potential pollutants in crude oils from specific locations (domestic and foreign).
- Background report developed entitled "Residuum and Residual Fuel Oil Supply and Demand in the United States...1973-1985."*
- Major environmental assessment contractor brought on board to identify environmental tradeoffs on all existing and projected processing/utilization options for residual oil.
- Contract negotiations initiated for comprehensive categorization and characterization of residual oils.
- Report issued by Radian entitled "Environmental Problem Definition for Petroleum Refineries, Synthetic Natural Gas Plants, and Liquefied Natural Gas Plants."

° Advanced Oil Processing (CAFB Development)--Demonstration at small to moderate commercial-scale of the chemically active fluid bed (CAFB) process for converting heavy high-sulfur, high-metals content residual oils to clean, high-temperature gaseous fuel. Significant accomplishments include:

- Success achieved in the pilot plant program with design work begun on demonstration of CAFB process on utility boiler as an environmentally sound fuel switching technique.
- Progress report issued entitled "Development of the Chemically Active Fluid Bed Process, A Status Report and Discussion." (See S. L. Rakes in Section 8.2.)
- Continuous operation of the CAFB pilot plant at Esso Petroleum, Ltd., for periods as long as 412 hours, with 212 hours between decaking or cleaning of the gas duct. Sulfur removal of 85

(*) All EPA reports cited in this document are more completely identified on Section 8.2

percent and vanadium retention of 100 percent on the bed material were based on the residual oil inputs.

- Pilot testing of coal feedstocks in the continuous CAFB pilot plant begun in support of the planned demonstration.
- Design/construction of a 10 MW demonstration plant at Central Power and Light (CPL), San Benito, Texas, underway with Foster Wheeler Corporation as prime contractor.
- Westinghouse control technology studies show that the trace metals sequestered by the bed material are bound tightly and will not leach out into the environment. The spent sorbent shows promise as a component of concrete. The spent bed material was found to contain very little, if any, organic compounds.

° Advanced Oil Processing (Control Technology Development)--Development and demonstration, where needed, of technologies for the removal of sulfur, nitrogen, and potentially hazardous trace materials from petroleum, petroleum derivatives, and other liquid fuels. Development and evaluation of the best practical control technologies for commercial or near-commercial processes.

- Determination of the fundamental characteristics of the reactions involved in simultaneous hydrodesulfurization and hydrodenitrogenation. Report issued entitled "Catalytic Desulfurization and Denitrogenation."

°° Identification of specific catalysts that tend to optimize demetallization of oils, and preliminary estimates of catalytic demetallization and desulfurization of specific Venezuelan, Soviet, and Iranian Oils. Phase III report issued entitled "Demetallization of Heavy Residual Oils."

°° Work initiated to optimize denitrogenation of residual oils.

1.3 List of Contractors/Grantees

The following organizations are carrying out work in the areas indicated:

° Environmental Assessment of the Uses of Residual Oils

Contractor: Catalytic, Inc.

Contract No.: 68-02-2155

° Chemically Active Fluid Bed Development and Support

Contractor: Esso Petroleum Company, England

Contract No.: 68-02-2159

° Preliminary Environmental Assessment of the CAFB Process; Coal and Lignite

Contractor: GCA Corporation

Contract No.: 68-02-2632

° Engineering Support for the Demonstration of Chemically Active Fluid Bed Process

Contractor: Westinghouse

Contract No.: 68-02-2142

° Demonstration of the Chemically Active Fluid Bed Process

Contractor: Foster Wheeler

Contract No.: 68-02-2106

° Analytical Support to Include Comprehensive Analysis of Hazardous Substances in Residual Oils

Contractor: Westinghouse

Contract No.: 68-02-2638

° HDS/HDN Interactions in Liquid Fuels

Grantee: MIT

Grant No.: R804123

° Control Technology for HDS/HDN of Liquid Fuels

Contractor: Hydrocarbon Research, Inc.

Contract No.: 68-02-0293

2. BACKGROUND

2.1 The Residual Oil Environmental Problem

The two primary environmental problems associated with residual oil are air pollution from its processing and combustion as a fuel, and water pollution from leakage and spills during its transport and handling.

Combustion of residual fuel oil produces gaseous and particulate emissions. Gaseous pollutants include oxides of sulfur and nitrogen and relatively smaller amounts of carbon monoxide, hydrocarbons, and aldehydes. Particulate emissions contain the trace elements originally present in the residual oil, such as vanadium, as well as unburned carbon and sulfates. Recent data indicate that residual oil containing vanadium may produce higher primary sulfate emissions than coal. [1] More data are needed to confirm this. Moreover, little is known about the toxicity of particulate emissions from residual oil compared to those from coal. The possibility exists that they are much more toxic than those from coal.

Leakage and spills of residual oil from oil transfer operations, tank cleaning, ballast disposal, tanker accidents, and other operations result in discharge of residual oils to the water and wet land environments. Residual oil contains relatively concentrated fractions of toxic substances which, besides being health and ecological hazards, are extremely slow to degrade. In addition, substances used as dispersants in cleaning up oil spills can also have undesirable effects.

Fuel oils are classified by the American Society for Testing and Materials (ASTM) into five grades, Nos. 1, 2, 4, 5, and 6. Nos. 1 and 2 are distillate oils for use in burners requiring a volatile or moderately volatile fuel, respectively. Nos. 4, 5 and 6 oils are marketed in the United States as residual fuel oils.[2] Nos. 4 and 5 are produced either as straight-run fractions or by blending No. 6 and No. 2. Their primary use is in space heating for large apartments and commercial buildings. No. 6 is the heaviest oil and is used in large industrial and electric utility boilers for process steam and power generation. It also is a fuel for marine engines and is then referred to as bunker fuel oil or Bunker C.

2.1.1 Amounts and Ways Residual Oil is Used in the U. S.

The U. S., with the exception of the East Coast, has historically relied on low-cost domestic supplies of natural gas and coal to meet its need for industrial and public utility energy resources. The East Coast, being physically separated from Western reserves of coal and Southern reserves of natural gas, developed a dependence on residual fuel oil from Caribbean refineries for use in public utility and industrial boilers.

In the sixties and early seventies, shortages of natural gas shifted domestic energy demand toward residual fuel oil and coal, causing more areas in the U. S. to join the East Coast's dependence on fuel oil imports. Over the period 1969-1972 annual domestic demand for fuel oil increased 203 x 10^6 bbl (32.3 x 10^6 m^3) from the 1969 demand of 722 x 10^6 bbl (115 x 10^6 m^3) to 925 x 10^6 bbl (147 x 10^6 m^3) in 1972. In response, fuel oil imports jumped 176 x 10^6 bbl (28 x 10^6 m^3) (38 percent)

to 637 x 10^6 bbl (101 x 10^6 m^3), while domestic production of fuel oil rose only from 28 x 10^6 bbl (4.5 x 10^6 m^3) (10 percent) to 293 x 10^6 bbl (46.6 x 10^6 m^3) per year. To counteract this trend, the U. S. Government initiated the Old Oil Entitlements and Oil Import Fee Program after 1972. The relative growth rates of fuel oil imports and domestic production were reversed in 1974. Under these programs domestic crude prices were pegged at a level well below the world crude market price, and a fee was levied on all crude oil and product imports. Caribbean refiners faced world prices for crude and potentially lower U. S. market prices for residual fuel oil. Due to the availability of low-cost domestic crude, U. S. refiners had the advantage of a composite crude oil cost that fell below world levels, and a residual fuel oil product price that was set by relatively high-priced Caribbean substitutes. Thus, there was an obvious economic incentive for domestic refiners to increase their fuel oil yield. From 1972 to 1974, U. S. demand for residual fuel oil rose 32 x 10^6 bbl (5 x 10^6 m^3) (48 percent) to a total of 390 x 10^6 bbl (62 x 10^6 m^3), while imports actually dropped 64 x 10^6 bbl (10 x 10^6 m^3) (10 percent) to a total of 574 x 10^6 bbl (91 x 10^6 m^3) per year.

The total supply of residual fuel oil was over 927 x 10^6 bbl (148 x 10^6 m^3) in 1972.[3] The supply of residual fuel oil by grades (No. 5 and No. 6 combined and No. 4), point of origin (domestic production and import), and sulfur levels is shown in Table 1. About two-thirds of the total U. S. supply was imported. Statistics on imports of residual fuel oil are shown in Table 2. The great majority of imports came from

TABLE 1. DOMESTIC PRODUCTION AND IMPORT OF RESIDUAL FUEL OIL BY SULFUR CONTENT FOR 1972[3]

Sulfur Content, Percent	Quantity, 1000 barrels ($m^3 \times 10^6$)[a]						
	No. 5 and No. 6 Fuel Oil			No. 4 Fuel Oil			
	Domestic Production	Import	Subtotal	Domestic Production	Import	Subtotal	Total
Zero-0.50	64,855 (10.3)	203,137 (32.3)	267,992 (42.7)	6,621 (1.1)	22,223 (3.5)	28,844 (4.6)	296,836 (47.2)
0.51-1.00	70,824 (11.3)	163,764 (26.1)	234,588 (37.3)	3,117 (0.5)	5,967 (0.9)	9,084 (1.5)	243,672 (38.7)
1.01-2.00	92,652 (14.8)	79,316 (12.6)	171,968 (27.4)	1,683 (0.3)	2,925 (0.5)	4,608 (0.7)	176,576 (28.1)
Over 2.00	64,188 (10.2)	145,447 (23.0)	209,635 (33.4)	609 (0.1)	133	742 (0.1)	210,377 (33.5)
	292,519 (46.6)	591,664 (94.0)	884,183(140.8)	12,030 (1.9)	31,248 (4.9)	43,278 (6.9)	927,461(147.5)

[a]Metric units may not add to totals because of rounding in conversion from barrels.

TABLE 2. IMPORTS OF RESIDUAL FUEL OILS BY SULFUR CONTENT FOR 1972[3]

Country	Quantity, 1000 barrels ($m^3 \times 10^6$)[a] Sulfur Content, percent				
	0-0.5	0.51-1.00	1.01-2.00	Over 2.00	Total
Venezuela	40,059 (6.4)	39,185 (6.2)	45,250 (7.2)	69,600 (11.1)	194,094 (30.9)
N.W.I.	21,878 (3.5)	34,868 (5.5)	7,734 (1.2)	47,988 (7.6)	112,468 (17.9)
Virgin Is.	56,785 (9.0)	29,669 (4.7)	660 (0.1)	9,134 (1.5)	96,248 (15.3)
Trinidad	13,243 (2.1)	24,193 (3.8)	14,033 (2.2)	5,105 (0.8)	56,574 (9.0)
Bahamas	33,491 (5.3)	9,339 (1.5)	8,960 (1.4)	1,825 (0.3)	53,615 (8.5)
Canada	8,864 (1.4)	9,936 (1.6)	1,593 (0.3)	8,265 (1.3)	28,658 (4.6)
Italy	17,198 (2.7)	11,143 (1.8)	87		28,428 (4.5)
Others	33,842 (5.4)	11,398 (1.8)	3,924 (0.6)	3,663 (0.6)	52,827 (8.4)
TOTAL	225,360 (35.8)	169,731 (27.0)	82,241 (13.1)	145,580 (23.1)	622,912 (99.0)

[a]Metric units may not add to totals because of rounding in conversion from barrels.

Venezuela and the Caribbean area. The available data indicate that only 4.7 percent of the total supply is No. 4 fuel oil. The breakdown of the remaining 95.3 percent between No. 5 and No. 6 is not available. Most of it probably is No. 6 fuel oil.

Domestic demand for residual fuel oil by consumption categories is shown in Table 3 for 1971 and 1972. The 1971 statistics were taken directly from published data. [4] The 1972 data were derived from the 1971 data assuming that: (1) the total demand is equal to the total supply in 1972, and (2) the percentage breakdown by consumption catetories is the same in 1971 and 1972. The difference between the supply and the demand is probably insignificant when small adjustments are made for export change in stocks. The major consumption categories are electric utilities, space heating for apartments and commercial buildings, industrial uses, and vessel bunkering. All of the No. 4 fuel oil probably is used for space heating of apartments and commercial buildings. Almost all of the residual oil is burned in boilers for the production of steam for various uses, such as heating, electric power generation, and vessel propulsion.

Since most of the residual fuel oil is used in boilers to generate steam for space heating, power generation, industrial process applications, and vessel propulsion, the primary source of pollution is steam boilers. No useful data could be found to break down the residual fuel oil demand in each consumption category by the type and size of boilers or other combustion process.

TABLE 3. DOMESTIC DEMAND FOR RESIDUAL FUEL OIL BY USES FOR 1971[4] AND 1972

Uses	1971 Quantity, 1000 bbl ($m^3 \times 10^6$)	1971 Percent	1972[a,b] Quantity, 1000 bbl ($m^3 \times 10^6$)
Heating Oils (apartments and commercial)	182,639 (29.0)	21.79	202,100 (32.1)
Industrial Uses (excluding refinery fuel)	135,469 (21.5)	16.17	150,000 (23.8)
Refinery Fuel (excluding heating oils)	32,626 (5.2)	3.89	36,100 (5.7)
Electric Utilities	371,820 (59.1)	44.37	411,400 (65.4)
Railroads	1,262 (0.2)	0.15	1,400 (0.2)
Military	29,217 (4.6)	3.49	32,400 (5.2)
Vessel Bunkering (excluding military)	78,727 (12.5)	9.39	87,100 (13.8)
Miscellaneous	6,285 (1.0)	0.75	7,000 (1.1)
TOTAL	838,045 (133.2)	100.00	927,500 (147.5)

[a]1972 figures were estimated based on 1971 figures.

[b]Metric units may not add to totals because of rounding in the conversion from barrels.

Industries use residual fuel oil primarily to raise steam which then is used for process and space heating, for power generation, and to drive equipment. A small fraction is used in direct-fired heaters and furnaces. In most cases, it is doubtful that an industry or a company has accurate knowledge of the ultimate fuel use. It is estimated that about 90 percent of the industrial residual fuel oils is used to raise steam for process and space heating, 5 percent for power generation, and 5 percent in direct-fired process heaters. In petroleum refineries, about 60 percent of residual fuel oil is probably consumed in fired process heaters and 40 percent to raise process steam. Refineries normally generate very little power but rely on purchased power.

Uses of residual fuel oil by railroads probably include space heating and possibly operation of tugboats owned by railroads. A major fraction of the military uses is probably as bunkering fuel by the Navy.

2.1.2 Contaminants in Residual Oils

The composition of residual fuel oils--with respect to the potentially polluting constituents, such as sulfur, nitrogen, trace elements and organics--depends largely on the crude oil from which the residual fuel oil comes. Characteristics of crude oils from major oil-producing regions are described in Table 4. It should be noted that the characteristics vary widely among the crude oils of a given region, or even a given country or an area. Generalization of crude oil characteristics nontheless serves to obtain a rough estimate of the polluting constituents in residual fuel oil.

TABLE 4. GENERAL CRUDE OIL CHARACTERISTICS BY REGION[5]

Region	Country	Area	Characteristics
North America	U.S.	California	Medium to high S, N, and trace elements
	U.S.	Midcontinent	Low S, N, and trace elements
	Canada	Alberta/B.C.	Similar to U.S. Midcontinent
South America	Venezuela	Lake Maracaibo	Medium to high S; high trace elements
Africa	Algeria, Libya Nigeria and other West African		Low S and trace elements but medium nitrogen in relation to S
Middle East	Saudi Arabia, Iran, etc.		High S and moderate trace elements
Asia	Indonesia		Low S, N, and trace elements

Sulfur

The sulfur content of residual fuel oil is reported in Mineral Industry Surveys published monthly by the Bureau of Mines. The latest annual statistics available for 1972 are shown in Table 1. Sulfur content is given by ranges. To estimate the total quantity of sulfur, a weighted average was estimated for each range based upon state and local regulations pertaining to fuel oil sulfur levels as follows:

(1) For the zero to 0.50 percent range, the weighted average was taken at 0.4 percent as an average of the established 0.3 and 0.5 percent limits.

(2) For 0.51 to 1.00 percent range, the weighted average was taken at the established 1.0 percent limit.

(3) For sulfur content above 1.0 percent, no fuel oil sulfur regulations exist. Therefore, weighted averages were assumed at 1.5 percent for the 1.01 to 2.00 percent range and at 2.4 percent for the over 2.00 percent range.

The total sulfur contents of residual fuel oil derived from the weighted averages of sulfur levels are shown in Table 5.

TABLE 5. TOTAL SULFUR CONTENT OF RESIDUAL FUEL OIL FOR 1972

Sulfur Content, Percent		Quantity of Sulfur, ton[a] (10^9g)[c]				
		No. 5 and No. 6 Fuel Oil		No. 4 Fuel Oil		
Range	Weighted Average[b]	Domestic	Import	Domestic	Import	Total
Zero-0.50	0.4	42,900 (38.9)	134,500 (122)	4,400 (4)	14,700 (13.3)	196,500 (178.3)
0.51-1.00	1.0	117,200 (106.3)	271,000 (245.8)	5,200 (4.7)	9,900 (9)	403,300 (365.9)
1.01-2.00	1.5	230,000 (208.7)	196,900 (178.6)	4,200 (3.8)	7,300 (6.6)	438,400 (397.7)
Over 2.00	2.4	255,000 (231.3)	577,700 (524)	2,400 (2.2)	500 (0.5)	835,600 (758)
TOTAL		645,100 (585.2)	1,180,100 (1,070.5)	16,200 (14.7)	32,400 (29.4)	1,873,800 (1699.9)

[a]Based upon a density of residual fuel oil at 331 lb/bbl (944 kg/m^3). (4)

[b]Estimated by Battelle.

[c]Metric units may not add to totals because of rounding in conversion from tons.

Nitrogen and Trace Elements

Data on nitrogen, trace elements, and fine particulates are not as readily available or complete as those on sulfur. Analyses of nitrogen, nickel, and vanadium for residual fuel oils produced from several crude oil sources are shown in Table 6. More extensive data on trace metals by grades of residual fuel oil are shown in Table 7. The data in Table 7 indicate no apparent correlations among the fuel oil grades, sulfur levels, and trace metal analyses. The following methodology was used for estimating the nitrogen and trace metal content of residual fuel oil:

(1) Nitrogen, nickel, and vanadium were estimated by breaking down the total residual fuel oil supply by crude oil sources and applying the analysis data for each source (Table 6).

(2) Other trace metals were estimated by taking the ratios relative to the sum of nickel and vanadium content for the entire residual fuel oil supply.

The breakdown of the residual oil supply by crude oil sources, and the quantities of nitrogen, nickel, and vanadium are shown in Table 8. The compositions of residual fuel oil were taken from Table 6. For the U. S., Venezuelan, and Middle East crude oils, average values of the composition data given in Table 6 were used. The compositions of the residual fuel oils from African and Indonesian crudes were estimated by Battelle. The concentrations of nitrogen, nickel, and vanadium averaged over the total residual fuel oil supply were estimated at 0.45 percent, 46 ppm, and 140 ppm, respectively.

TABLE 6. TYPICAL SULFUR, NITROGEN, AND TRACE METAL ANALYSES OF RESIDUAL FUEL OIL

Crude Source	Sulfur, percent	Nitrogen, percent	Nickel, ppm	Vanadium, ppm	Reference
Domestic	4.0	0.53	45	138	(5)
Venezuelan	2.6	0.61	94	218	(5)
Venezuelan (Tijuana)	2.2	--	39	200	(6)
Middle East	5.2	0.41	58	167	(5)
Middle East (Kuwait)	4.4	0.26	14	50	(5)
Middle East	4.3	0.16	9	32	(5)
Middle East	2.6	0.37	57	88	(5)
Middle East	4.1	0.29	48	127	(5)
Middle East (Kuwait)	4.1	0.23	19	53	(6)

TABLE 7. TYPICAL SULFUR AND TRACE METAL ANALYSES OF RESIDUAL FUEL OIL[6]

Fuel Oil Grade	No. 4			No. 5			No. 6				
Type	A	B	C	A	B	E	F	B	C	H	G
Sulfur, percent	0.58	0.57	1.90	0.59	0.69	1.90	0.69	0.78	2.36	3.07	3.95
Trace Metals, ppm											
Al	0.6	4	4	4	20	5	4	40	10	30	1.5
Ca	0.3	3	2.8	2.5	1	4	5	3	7	4	1
Cu	0.05	0.04	--	0.3	0.3	0.1	0.3	0.5	--	0.4	0.04
Fe	4	1	1.2	15	10	8	20	40	3	5	0.6
Pb	1	0.9	--	10	3	2	3	9	--	8	0.4
Mg	0.6	1	19	5	1	9	5	4	47	10	1
Mn	0.08	0.1	--	0.5	0.3	0.5	0.7	1	--	0.7	--
Ni	0.2	--	8	10	10	20	10	20	20	20	12
K	0.09	--	0.4	0.4	5	0.1	1	1	1	1	0.2
Si	1	2	2.4	4.0	30	4	3	40	6	20	5.7
Na	0.4	4	10	6.5	5	14	17	11	26	14	4.0
Sn	0.3	0.3	--	1.5	0.4	--	--	--	--	0.3	--
V	0.7	4	167	3.5	11	71	8	14	417	110	40
Zn	--	4	--	--	--	--	--	--	--	--	--

TABLE 8. NITROGEN, NICKEL, AND VANADIUM CONTENT OF RESIDUAL FUEL OIL

[d]Source of Crude Oil	Residual Fuel Oil Produced		Polluting Constituents in Residual Fuel Oil					
	10^3 barrels (10^6 m^3)	10^3 tons (10^{12} g)	Nitrogen[c] percent	Nickel[c] tons (10^9 g)	Nickel[c] ppm	Vanadium[c] tons (10^9 g)	Vanadium[c] ppm	Vanadium[c] tons (10^9 g)
U. S. and Canada[a]	243,979 (38.8)	40,379 (36.6)	0.53	214,000 (194.1)	45	1,820 (1.65)	138	5,570 (5.05)
Venezuela[a]	392,235 (62.4)	64,915 (58.9)	0.61	396,000 (359.2)	67	4,350 (3.95)	209	13,570 (12.31)
Middle East[a]	120,048 (19.1)	19,868 (18)	0.29	58,000 (52.6)	34	680 (0.62)	86	1,710 (1.55)
Africa[b]	120,048 (19.1)	19,868 (18)	0.10	20,000 (18.1)	10	200 (0.18)	20	400 (0.36)
Indonesia[b]	51,151 (8.1)	8,465 (7.6)	0.10	8,000 (7.25)	10	80 (0.07)	20	170 (0.15)
TOTAL	927,461 (147.5)	153,495 (139.2)		696,000 (631.4)		7,130 (6.47)		21,420 (19.43)

[a]Contaminant analyses based on data given in Table 7.

[b]Contaminant analyses estimated by Battelle.

[c]Average concentrations were estimated at: N = 0.45 percent (750 tons/10^6 barrels) (4.28 kg/m^3)
Ni = 46 ppm (7.7 tons/10^6 barrels) (43.97 g/m^3)
V = 140 ppm (23 tons/10^6 barrels) (131.27 g/m^3)

[d]Metric units may not add to totals because of rounding in conversion from reported units.

Concentrations of other trace elements were estimated by taking the ratios relative to the sum of nickel and vanadium content (i.e., weight of trace element per weight of Ni + V). Data were compiled from direct analysis of residual fuel oil (data for No. 6 fuel oil in Table 7), crude oil analysis, [5] analysis of particulate emissions from combustion of a No. 6 fuel oil, [7] and other sources. [8,9,10] Results for trace metal content of residual fuel oil are summarized in Table 9.

Organics

The nature of the organic fractions found in burning residual oil is primarily polycyclic organic matter (POM) and CO; these potentially hazardous pollutants result from incomplete combustion.[13] The POM class includes polynuclear aromatic hydrocarbons commonly identified as PNA or PAH, and nitrogen-containing heterocyclic compounds. Although the physical states of POM and soot are different, they probably have common origins and similar chemical reactivity. The materials labeled POM are emitted in small or trace quantities during the combustion of residual oil. Studies of the mode of formation and destruction of POM in the combustion process are difficult to carry out because of the very low concentrations, the lack of simple analytical procedures for identifying them, and the large number of individual compounds making up this class of material. Typical POM that have been observed are anthracene, pyrene, methyl anthracene, fluoranthene, methyl fluoranthenes/pyrenes, chrysene, perylene, benzo(ghi)perylene, and coronene.

2.1.3 Emission Standards

Current emission standards for SO_2, NO_x, and particulates from oil-fired boilers are 1.2 (0.516), 0.70 (0.3), and 0.10 (0.04 kg) lb per 10^6 Btu (GJ), respectively.

TABLE 9. ESTIMATED TRACE METAL ANALYSES OF RESIDUAL FUEL OIL

Element	Concentration ppm	Concentration ton/10^6 barrels (g/m^3)		Percent of Total Metal Content	Reference
Fe	19	3.1	(17.69)	5.6	(8)
B	0.9	0.15	(0.856)	0.27	(9)
Si	21	3.5	(19.97)	6.4	(8)
Mg	19	3.1	(17.69)	5.6	(8)
Mn	2.5	0.41	(2.34)	0.75	(8)
Pb	16	2.6	(14.84)	4.7	(8)
Al	24	4.0	(22.82)	7.3	(8)
Mo	0.13	0.022	(0.136)	0.040	(9)
Cu	1.0	0.17	(0.970)	0.31	(8)
Ca	5.4	0.89	(5.08)	1.6	(8)
Cr	1.5	0.25	(1.43)	0.45	(9)
Ba	2.5	0.41	(2.34)	0.75	(9)
Co	7.7	1.3	(7.42)	2.4	(9)
K	1.2	0.20	(1.14)	0.36	(8)
Sn	0.4	0.066	(0.377)	0.12	(8)
Ag	0.4	0.066	(0.377)	0.12	(9)
Na	20	3.3	(18.83)	6.0	(8)
Zn	0.9	0.15	(0.856)	0.27	(9)
Ti	1.5	0.25	(1.43)	0.45	(9)
As	0.22	0.036	(0.205)	0.065	(5)
Sb	0.54	0.089	(0.508)	0.16	(5)
Hg	0.05	0.0083	(0.0047)	0.015	(10)

TABLE 9. ESTIMATED TRACE METAL ANALYSES OF RESIDUAL FUEL OIL (continued)

Element	Concentration ppm	Concentration ton/10^6 barrels (g/m^3)	Percent of Total Metal Content	Reference
Se	2.4	0.40 (2.28)	0.73	(11,12)
Ni	46	7.6 (43.37)	13.8	(Table 8)
V	140	23 (131.24)	41.8	(Table 8)
TOTAL	334	55 (313.83)	100.1	

2.2 Definition of Environmental Assessment and Control Technology Development

An environmental assessment, as defined for IERL-RTP studies of fossil energy processes, is a continuing iterative study aimed at:

(1) determining the comprehensive multimedia environmental loadings and environmental control costs, from the application of the existing and best future definable sets of control/disposal options, to a particular set of sources, processes, or industries; and

(2) comparing the nature of these loadings with existing standards, estimated multimedia environmental goals, and bioassay specifications as a basis for prioritization of problems/control needs and for judgment of environmental effectiveness.

Figure 1 includes a more comprehensive delineation of environmental assessment in the form of a flow schematic.

The overall nature of control technology development is depicted in Figure 2.

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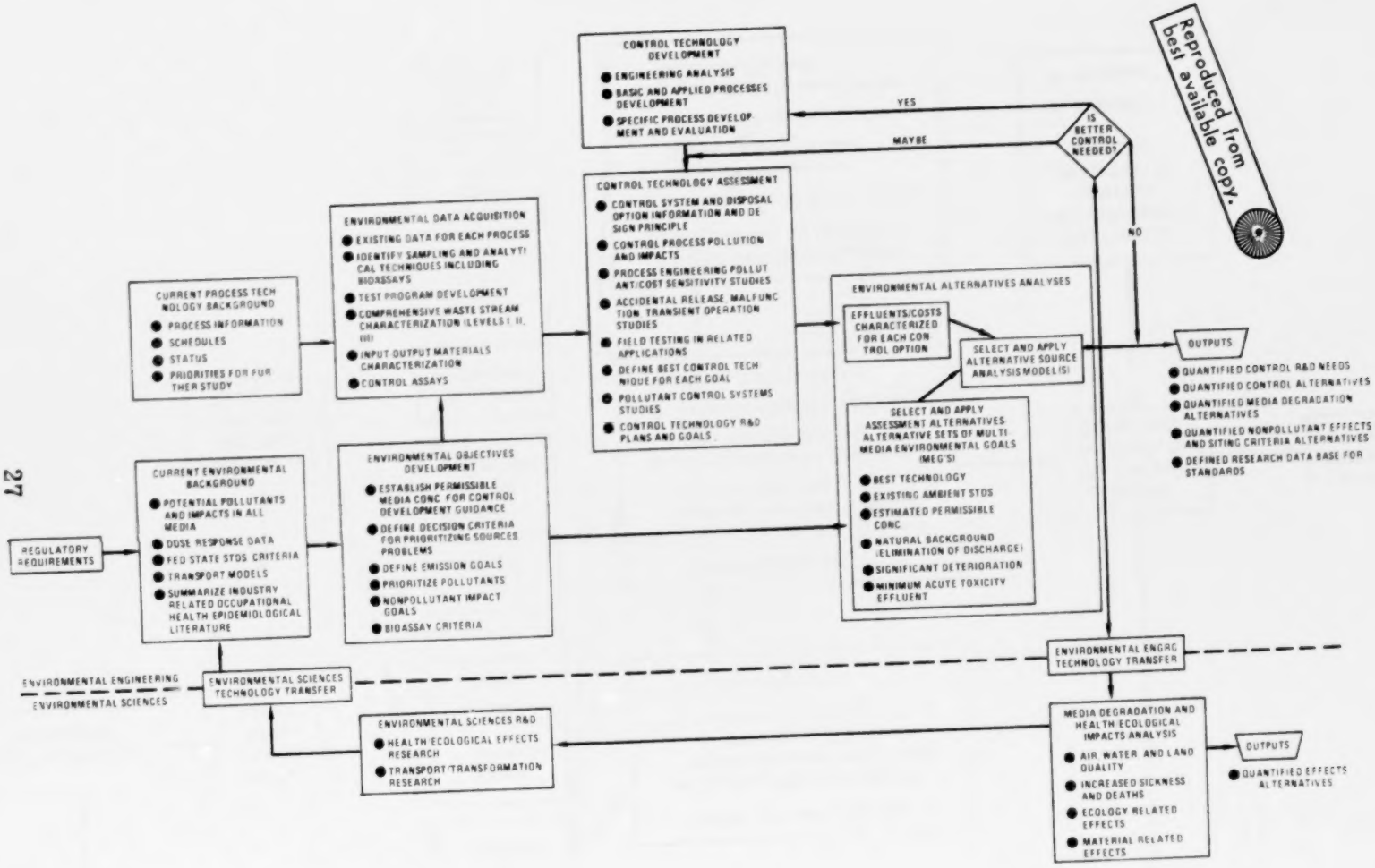
CONTROL TECHNOLOGY DEVELOPMENT
ENGINEERING ANALYSIS
BASIC AND APPLIED PROCESSES DEVELOPMENT
SPECIFIC PROCESS DEVELOPMENT AND EVALUATION
YES
MAYBE
IS BETTER CONTROL NEEDED?
NO
ENVIRONMENTAL DATA ACQUISITION
EXISTING DATA FOR EACH PROCESS
IDENTIFY SAMPLING AND ANALYTICAL TECHNIQUES INCLUDING BIOASSAYS
TEST PROGRAM DEVELOPMENT
COMPREHENSIVE WASTE STREAM CHARACTERIZATION (LEVELS I, II, III)
INPUT OUTPUT MATERIALS CHARACTERIZATION
CONTROL ASSAYS
CONTROL TECHNOLOGY ASSESSMENT
CONTROL SYSTEM AND DISPOSAL OPTION INFORMATION AND DESIGN PRINCIPLE
CONTROL PROCESS POLLUTION AND IMPACTS
PROCESS ENGINEERING POLLUTANT/COST SENSITIVITY STUDIES
ACCIDENTAL RELEASE MALFUNCTION TRANSIENT OPERATION STUDIES
FIELD TESTING IN RELATED APPLICATIONS
DEFINE BEST CONTROL TECHNIQUE FOR EACH GOAL
POLLUTANT CONTROL SYSTEMS STUDIES
CONTROL TECHNOLOGY R&D PLANS AND GOALS
ENVIRONMENTAL ALTERNATIVES ANALYSES
EFFLUENTS/COSTS CHARACTERIZED FOR EACH CONTROL OPTION
SELECT AND APPLY ALTERNATIVE SOURCE ANALYSIS MODEL(S)
SELECT AND APPLY ASSESSMENT ALTERNATIVES ALTERNATIVE SETS OF MULTI MEDIA ENVIRONMENTAL GOALS (MEG'S)
BEST TECHNOLOGY
EXISTING AMBIENT STDS
ESTIMATED PERMISSIBLE CONC
NATURAL BACKGROUND (ELIMINATION OF DISCHARGE)
SIGNIFICANT DETERIORATION
MINIMUM ACUTE TOXICITY EFFLUENT
OUTPUTS
QUANTIFIED CONTROL R&D NEEDS
QUANTIFIED CONTROL ALTERNATIVES
QUANTIFIED MEDIA DEGRADATION ALTERNATIVES
QUANTIFIED NONPOLLUTANT EFFECTS AND SITING CRITERIA ALTERNATIVES
DEFINED RESEARCH DATA BASE FOR STANDARDS
CURRENT PROCESS TECHNOLOGY BACKGROUND
PROCESS INFORMATION
SCHEDULES
STATUS
PRIORITIES FOR FURTHER STUDY
CURRENT ENVIRONMENTAL BACKGROUND
POTENTIAL POLLUTANTS AND IMPACTS IN ALL MEDIA
DOSE RESPONSE DATA
FED STATE STDS CRITERIA
TRANSPORT MODELS
SUMMARIZE INDUSTRY RELATED OCCUPATIONAL HEALTH EPIDEMIOLOGICAL LITERATURE
ENVIRONMENTAL OBJECTIVES DEVELOPMENT
ESTABLISH PERMISSIBLE MEDIA CONC FOR CONTROL DEVELOPMENT GUIDANCE
DEFINE DECISION CRITERIA FOR PRIORITIZING SOURCES PROBLEMS
DEFINE EMISSION GOALS
PRIORITIZE POLLUTANTS
NONPOLLUTANT IMPACT GOALS
BIOASSAY CRITERIA
REGULATORY REQUIREMENTS
ENVIRONMENTAL ENGINEERING
ENVIRONMENTAL SCIENCES
ENVIRONMENTAL SCIENCES TECHNOLOGY TRANSFER
ENVIRONMENTAL ENGRG TECHNOLOGY TRANSFER
ENVIRONMENTAL SCIENCES R&D
HEALTH/ECOLOGICAL EFFECTS RESEARCH
TRANSPORT/TRANSFORMATION RESEARCH
MEDIA DEGRADATION AND HEALTH/ECOLOGICAL IMPACTS ANALYSIS
AIR, WATER AND LAND QUALITY
INCREASED SICKNESS AND DEATHS
ECOLOGY RELATED EFFECTS
MATERIAL RELATED EFFECTS
OUTPUTS
QUANTIFIED EFFECTS ALTERNATIVES

Figure 1. Environmental assessment/control technology development diagram.

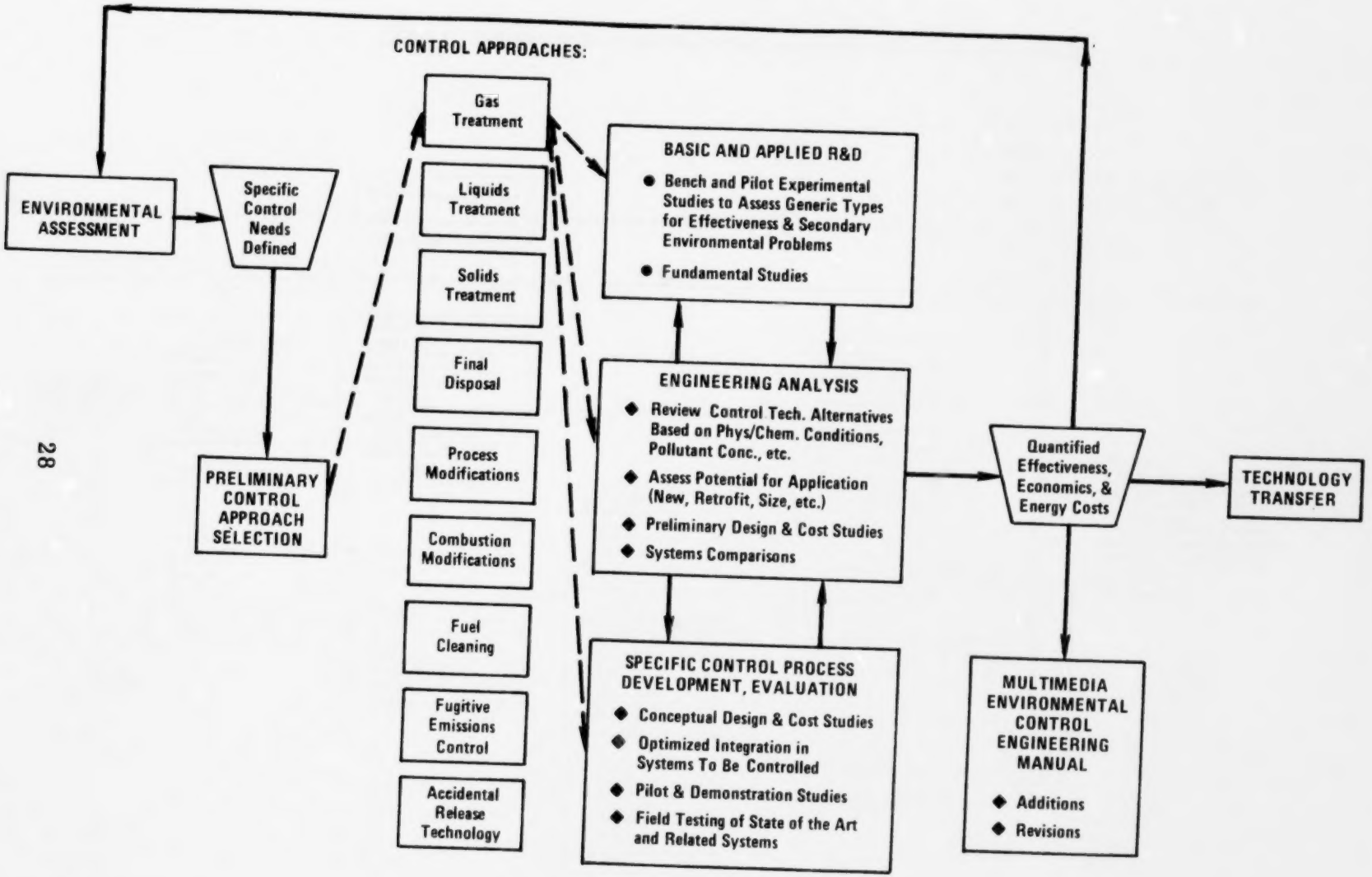
CONTROL APPROACHES:
ENVIRONMENTAL ASSESSMENT
Specific Control Needs Defined
PRELIMINARY CONTROL APPROACH SELECTION
Gas Treatment
Liquids Treatment
Solids Treatment
Final Disposal
Process Modifications
Combustion Modifications
Fuel Cleaning
Fugitive Emissions Control
Accidental Release Technology
BASIC AND APPLIED R&D
Bench and Pilot Experimental Studies to Assess Generic Types for Effectiveness & Secondary Environmental Problems
Fundamental Studies
ENGINEERING ANALYSIS
Review Control Tech. Alternatives Based on Phys/Chem. Conditions, Pollutant Conc., etc.
Assess Potential for Application (New, Retrofit, Size, etc.)
Preliminary Design & Cost Studies
Systems Comparisons
SPECIFIC CONTROL PROCESS DEVELOPMENT, EVALUATION
Conceptual Design & Cost Studies
Optimized Integration in Systems To Be Controlled
Pilot & Demonstration Studies
Field Testing of State of the Art and Related Systems
Quantified Effectiveness, Economics, & Energy Costs
MULTIMEDIA ENVIRONMENTAL CONTROL ENGINEERING MANUAL
Additions
Revisions
TECHNOLOGY TRANSFER

Figure 2. Control technology development diagram.

2.3 Alternatives for Residual Oil Combustion/Utilization/Control

Pollution control alternatives for stationary sources using residual oil can be grouped into the following categories:

- Direct Combustion With or Without Particulate Control
- Direct Combustion With Flue Gas Desulfurization
- Direct Combustion in Fluid Bed of Limestone at Atmospheric Pressure (AFBC)
- Partial Combustion at Atmospheric Pressure--Partial Oxidation (POX) Followed by Cleanup and Conventional Combustion
- Partial Combustion in a Chemically Active Fluid Bed (CAFB) Followed by Conventional Combustion
- Direct Hydrodesulfurization (HDS) of Residual Oil for Combustion
- Upgrading of Residual Oil Followed by HDS and Conventional Combustion

2.3.1 Direct Combustion With or Without Particulate Control

This category depends on crude oil low enough in sulfur so that the residual oil remaining after refining is low in sulfur and will meet standards when burned with no controls. Where particulate control is necessary, both baghouse filters (fiberglass) and electrostatic precipitators (ESPs) have been used; however, these collectors do not exhibit high collection efficiencies in the submicron range. Though the weight of these fines is not appreciable they do contribute significantly to visible emissions. [14] While the theoretical efficiency of the ESP

is quite high, the average operating efficiency is found to be much lower. The shorting out of one electrode can cause an entire section of electrodes to go out of service. Component failure of this kind cannot be corrected until the unit is removed from service. Day-to-day fluctutations of the dust resistivity can result in lowering the efficiency. This can be caused by variations in the SO_3 concentration which acts as a catalyst in the collection mechanism or the moisture content of the flue gas.[15] For these reasons, baghouse filters would be preferred over ESPs.[16]

2.3.2 Direct Combustion With Flue Gas Desulfurization

Flue gas desulfurization (FGD) processes are generally of the throwaway type, which produce an unusable mixture of sulfur compounds, or regenerable processes which can ultimately produce either elemental sulfur or sulfuric acid as a by-product. Elemental sulfur is normally preferred because it is a non-corrosive solid which is easily handled, stored, and shipped.

Non-Slurry Processes

- Sodium Solution Scrubbing -- SO_2 Regeneration and Reduction to Sulfur

Stack gas is washed with water in a venturi scrubber for removal of particulates and then washed in a spray scrubber with a recirculating solution of sodium salts in water for SO_2 removal. Makeup sodium carbonate is added to cover handling and oxidation losses of sodium sulfite and sulfate. Sodium sulfate crystals are purged from the system, dried, and sold. Water is evaporated from the scrubbing solution using a

single-effect evaporator to crystallize and thermally decompose sodium bisulfite, driving off concentrated SO_2. The resulting sodium sulfite is recycled to the scrubber and the SO_2 is reacted with methane for reduction to elemental sulfur. The regeneration and reduction areas are designed as a cyclic absorption/desorption process for removing SO_2 from waste gases and producing a concentrated SO_2 gas for feed to a contact sulfuric acid plant or to a Claus sulfur plant.

° Ammonia Process

Flue gas is passed through a scrubbing tower and SO_2 is absorbed by an aqueous stream of ammonium hydroxide, bisulfite, and sulfite. Makeup ammonia is injected into the flue gas ahead of the scrubber. The scrubber effluent is filtered to remove sludge and then aerated to oxidize the ammonium sulfite to ammonium sulfate. The ammonium sulfate is crystallized in an evaporator and then centrifuged and dried.

° Aluminum Sulfate Process

Flue gas, after the acid mist has been removed, is sent to an absorption tower where SO_2 is absorbed by a basic aluminum sulfate solution. The enriched solution goes to a regenerator and SO_2 is stripped off by steam heating. The SO_2 stream is dried and returned to the sulfuric acid plant. A side stream of enriched solution is reacted with calcium carbonate to prevent buildup of SO_3 in the absorbent. The calcium sulfate is removed by filtration.

Slurry Processes

° Limestone Slurry Scrubbing

Stack gas is washed with a recirculating slurry (pH of 5.8-6.4) of limestone and reacted calcium salts in water, using a two-stage (venturi and mobile bed) scrubber system for particulate and SO_2 removal. Limestone feed is ground wet prior to addition to the scrubber effluent hold tank. Calcium sulfite and sulfate salts are withdrawn to a disposal area for discard. Reheat of stack gas to 175°F (80°c) is provided.

° Lime Slurry Scrubbing

Stack gas is washed with a recirculating slurry (pH of 6.0-8.0) of calcined limestone (lime) and reacted calcium salts in water using two stages of venturi scrubbing. Lime is purchased from a nearby calcination operation, slaked, and added to both circulation streams. Calcium sulfite and sulfate are withdrawn to a disposal area for discard. Reheat of stack gas to 175°F (80°C) is provided.

° Magnesia Slurry Scrubbing -- Regeneration to H_2SO_4

Stack gas is washed using two separate stages of venturi scrubbing--the first utilizing water for removal of particulates, and the second utilizing a recirculating slurry (pH of 7.5-8.5) of magnesia (MgO) and reacted magnesium-sulfur salts in water for removal of SO_2. Makeup magnesia is slaked and added to cover only handling losses, since the sulfates formed are reduced during regeneration. Slurry from the SO_2

scrubber is dewatered, dried, calcined, and recycled during which concentrated SO_2 is evolved to a contact sulfuric acid plant producing 98 percent acid.

2.3.3 Direct Combustion in Fluid Bed of Limestone (AFBC)

To assess the removal of SO_2 from combustion gases when residual fuel oil is burned in a fluidized bed of sulfated lime with continuous feeding of limestone additive, experiments were performed in a 6-in. (15.2 cm) diameter fluidized-bed combustor at a variety of operating conditions. Residual fuel oil (containing 1.9% S) was burned in an excess of oxygen at bed temperatures ranging from 1450 to 1650°F (790 to 900°C), Ca/S mole ratios up to 11.9, a gas velocity of ~3 ft/sec (0.91 m/sec) (except for one experiment at 5.5 ft/sec [1.68 m/sec]), and with 3 vol % oxygen in the flue gas (except in one experiment with 1 vol % oxygen in the flue gas).

Table 10 lists operating data, concentrations of some components of the flue gas, and calculated sulfur retention and combustion efficiency data for the experiments in which limestone was fed to the combustor.

2.3.4 Partial Combustion at Atmospheric Pressure--Partial Oxidation (POX) Followed by Cleanup and Conventional Combustion

Over 100 commerical Partial Oxidation Units are now in successful operation around the world. Over half of these are charging residual fuel oil, with many others on crude oil. Others operate on light oil, naphtha, and natural gas. There is only one commercial unit in the

TABLE 10

OPERATING DATA AND RESULTS, COMBUSTION OF RESIDUAL FUEL OIL IN EXCESS AIR

Equipment: ANL 6-in. (150 mm) dia fluidized-bed combustor

Oil: Esso residual fuel oil, 1.97 wt % sulfur

Additive: Limestone No. 1359, as received (94.8 wt % $CaCO_3$, 0.9 wt % $MgCO_3$, 609 μm average particle size)

Starting Fluidized Bed: 17.3 lb (7,850 g) partially sulfated and calcined limestone No. 1359 (~24-in. (600 mm) fluidized-bed depth) Note: The final bed from a run was used as the starting bed for the following run.

O_2 Concentration in Flue Gas: ~3% (except 4A-1, 1%)

Experiment Oil	Fluidized-Bed Temp (°F)	(°C)	Oil Feed Rate (lb/hr)	(g/s)	Limestone Feed Rate (lb/hr)	(g/s)	Ca/S Mole Ratio	Gas Velocity (ft/sec)	(m/s)	Flue Gas Composition SO_2 (ppm)	NO (ppm)	CO (ppm)	CH_4 (ppm)	CO_2 (%)	Sulfur Retention (%)	Combustion Efficiency (%)
2	1650	(900)	5.8	(0.73)	0.6	(0.08)	1.6	5.5	(1.68)	1350	135	8500	>3400	No Data	16	<92
3A	1550	(840)	3.3	(0.42)	0.8	(0.1)	4.1	3.2	(0.98)	630	110	6000	1500	14.4	60	95
3B	1550	(840)	3.0	(0.38)	2.2	(0.28)	11.9	3.2	(0.98)	170	140	6000	800	15.0	90	94
3C	1550	(840)	3.3	(0.42)	1.1	(0.14)	5.4	3.0	(0.91)	200	150	5000	1200	14.2	88	No Data
4A	1450	(790)	3.2	(0.40)	1.2	(0.15)	6.0	3.1	(0.94)	350	140	5000	1100	15.0	78	95
4B	1650	(900)	3.2	(0.40)	1.2	(0.15)	6.0	3.1	(0.94)	550	130	5000	1000	14.0	66	96
4A-1	1450	(790)	4.8	(0.60)	1.2	(0.15)	4.0	3.3	(1.0)	520	190	>12000	>3400	No Data	68	No Data

Continental United States. This unit charges residual fuel oil and produces hydrogen. Another unit is operating on mixed feeds in Puerto Rico. Two additional units are planned for completion in the near future.

Essentially, any residual fuel oil or lighter hydrocarbon can be charged. The residual fuel oil is partially oxidized to form a gaseous mixture of carbon monoxide (CO) and hydrogen (H_2) with a small amount of methane (CH_4). Either oxygen (O_2) or air ($O_2 + N_2$) can be used for the partial oxidation. Some carbon dioxide (CO_2) and carbon soot (C) are formed as by-products. When air is used, the nitrogen remains in the gas product. When oxygen is used, the peak temperatures are usually controlled by a diluent such as steam or carbon dioxide. Carbon soot is produced as a result of incomplete combustion.

Residual fuel oil contains hydrocarbons and certain contaminants such as sulfur (S), nitrogen (N), ash, and various metals, which are mainly sodium (Na), vanadium (V) and nickel (Ni). The sodium is usually reduced to a sufficiently low level by crude oil desalting before the residue is fed to the reactor. Excessive sodium could damage the reactor lining. Some of the ash components, including vanadium and nickel compounds, along with some hydrogen cyanide (HCN), ammonia (NH_3), and any formic acid (HCO_2H) formed, are removed from the product gas in a water scrubber, since they are either soluble or suspended in water. The carbon soot remains in suspension in the water and can be removed by naphtha extraction or other recovery methods. The soot may then be recycled to the reactor for further reaction. Some ash is removed from the reactor as friable slag during shutdown for inspection. The sulfur products are only slightly soluble in water and therefore remain in

the product gas stream as hydrogen sulfide (H_2S), with some carbonyl sulfide (COS) and a trace of carbon disulfide (CS_2).

Several commercial processes are reported to be available for removal of up to 99+ percent of the H_2S from the product gas. Some processes selectively remove the H_2S, leaving much of the CO_2 in the gas. The CO_2 is desirable when using the gas as fuel to a gas turbine. By removal of much of the CO_2, using other absorbents, the product gas will have a higher Btu content.

The desulfurized product gas with essentially all the CO_2 removed will have a higher heating value (320 to 325 Btu/scf [9.56 to 9.71 kJ/M^3]) when O_2 is used for the oxidation. By comparison, the product from air oxidation will have a heating value of 120 to 125 Btu/scf (3.58 to 3.73 kJ/m^3) because of the nitrogen remaining in the gas. Because O_2 is more costly than air, the product gas from O_2 partial oxidation is more costly per 10^6 Btu (10^9 J) produced.

2.3.5 Partial Combustion in a Chemically Active Fluid Bed (CAFB) Followed by Conventional Combustion

The Chemically Active Fluid Bed (CAFB) process uses a shallow fluidized bed of lime or like material to produce a clean, hot gaseous fuel from heavy high-sulfur feedstocks, such as residual oils or refinery bottoms. Fuels which are normally solid, such as coal, have also been tested. The CAFB performs three operations simultaneously: (1) gasification and/or cracking of the feedstock; (2) removal of sulfur; (3) removal of

vanadium and other metals. The sulfur, vanadium, and other metals are captured by the CAFB. The CAFB has operated at temperatures in the range of 1600 to 1700°F (870 to 930°C) for that portion of the bed receiving the feedstock, commonly called the gasifier. The necessary heat release to maintain this temperature in the gasifier is accomplished by partial combustion of the feedstock. Flue gas recycle has been used to control the bed temperature. The amount of air to the CAFB is about 20 percent of that required for complete combustion of the feedstock, and is varied from this percentage to match the attributes of the feedstock to the capabilities of the process.

As the feedstock is gasified, the sulfur is captured by the CAFB as calcium sulfide, because the reaction occurs in an oxygen deficient or reducing atmosphere. The bed material is then moved, via fluidization, to the regenerator section of the reaction vessel. In current practice, this regenerator section is separated from the gasifier portion by a refractory divider and has a separate plenum or air passage to supply air for the regeneration reaction. The regeneration reaction is accomplished by passing air through the fluid bed. The calcium sulfide in the bed is oxidized to sulfur dioxide and calcium oxide. A minor amount of calcium sulfate is also produced during the regeneration step. The heat required to sustain the regeneration reaction at about 1500°F (815°C) is produced by the oxidation of the calcium sulfide with a contribution from the oxidation of carbon deposited on the surface of the bed material. The gaseous stream from the regenerator contains 6 to 10 percent, by volume, of SO_2 with 1 to 4 percent CO_2 and virtually no oxygen. This gas stream can be converted to either elemental sulfur or other products using existing technology. The regenerated bed material

is returned, via fluidization, to the gasifier portion of the vessel and the cycle is repeated.

The clean, hot product gas for the gasifier is ducted, through cyclones, to a boiler and burned in the normal manner, using burners designed specifically for the hot low-heating-value product gas.

From the above description, the basic areas of the CAFB process can be described as: (1) a fluid lime-bed particle combustor or gasifier; (2) an air blown regenerator; (3) solids transfer, makeup, and withdrawal; (4) fuel (feedstock) supply; (5) air supply; and (6) product gas ducting.

The process, as developed under U. S. Environmental Protection Agency (EPA) sponsorship, operates at atmospheric pressure. Pressure differentials throughout the system are required to induce fuel and materials flow and are on the order of those found in conventional boiler systems; that is on the order of 10 kPa. Figure 3 is a line diagram of the CAFB flow plan, and Figure 4 is a photograph of the Esso England Continuous CAFB Pilot Plant.

2.3.6 Direct Hydrodesulfurization (HDS) of Residual Oil for Combustion

The rapid growth of energy consumption in heavily industrialized countries, such as Japan and the United States, has created a large demand for heavy fuel oils. The increase in consumption created a rise in ambient SO_2 concentrations. To reduce the environmental impact of the

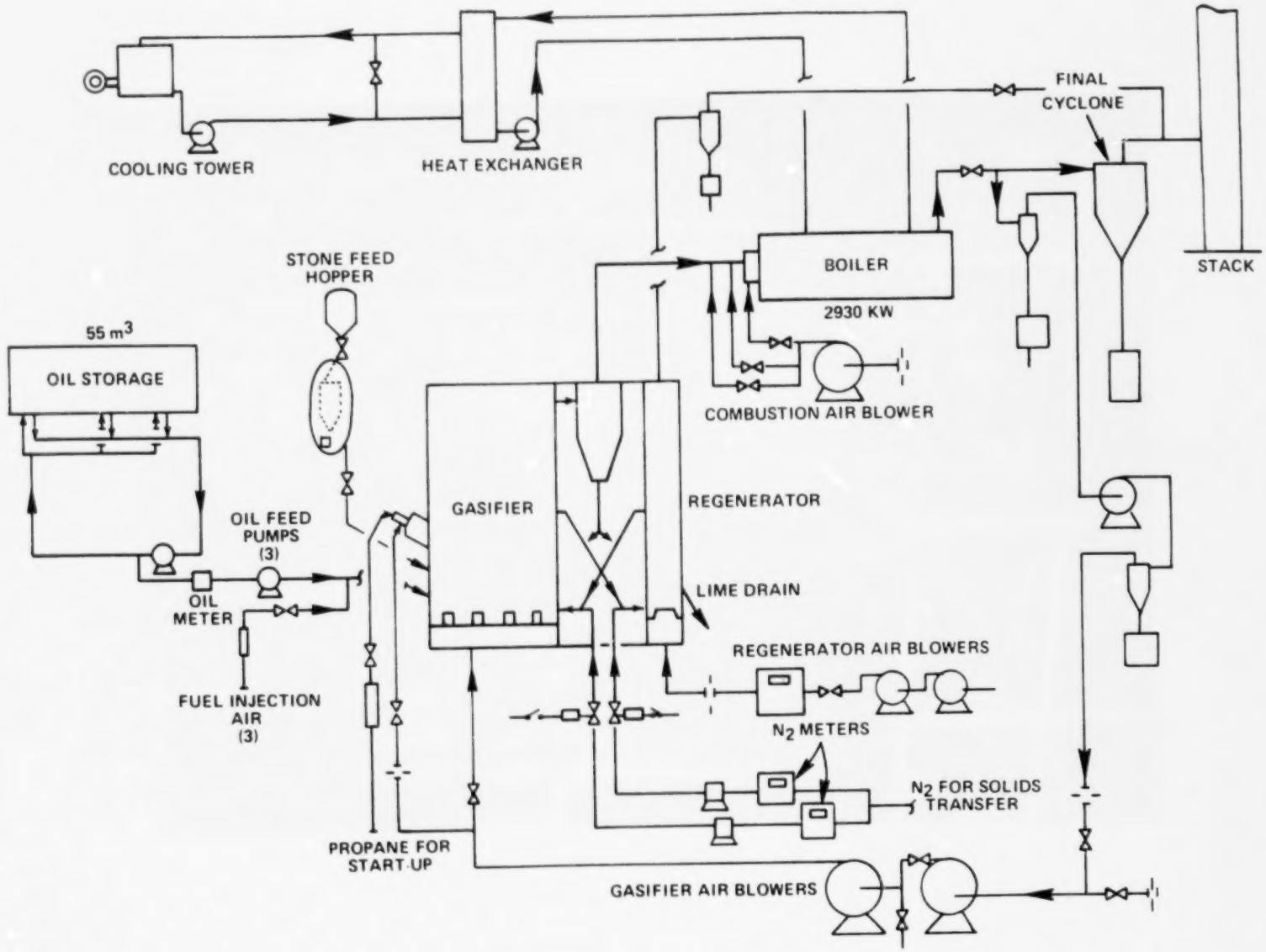

Figure 3. CAFB continuous pilot plant flow plan.

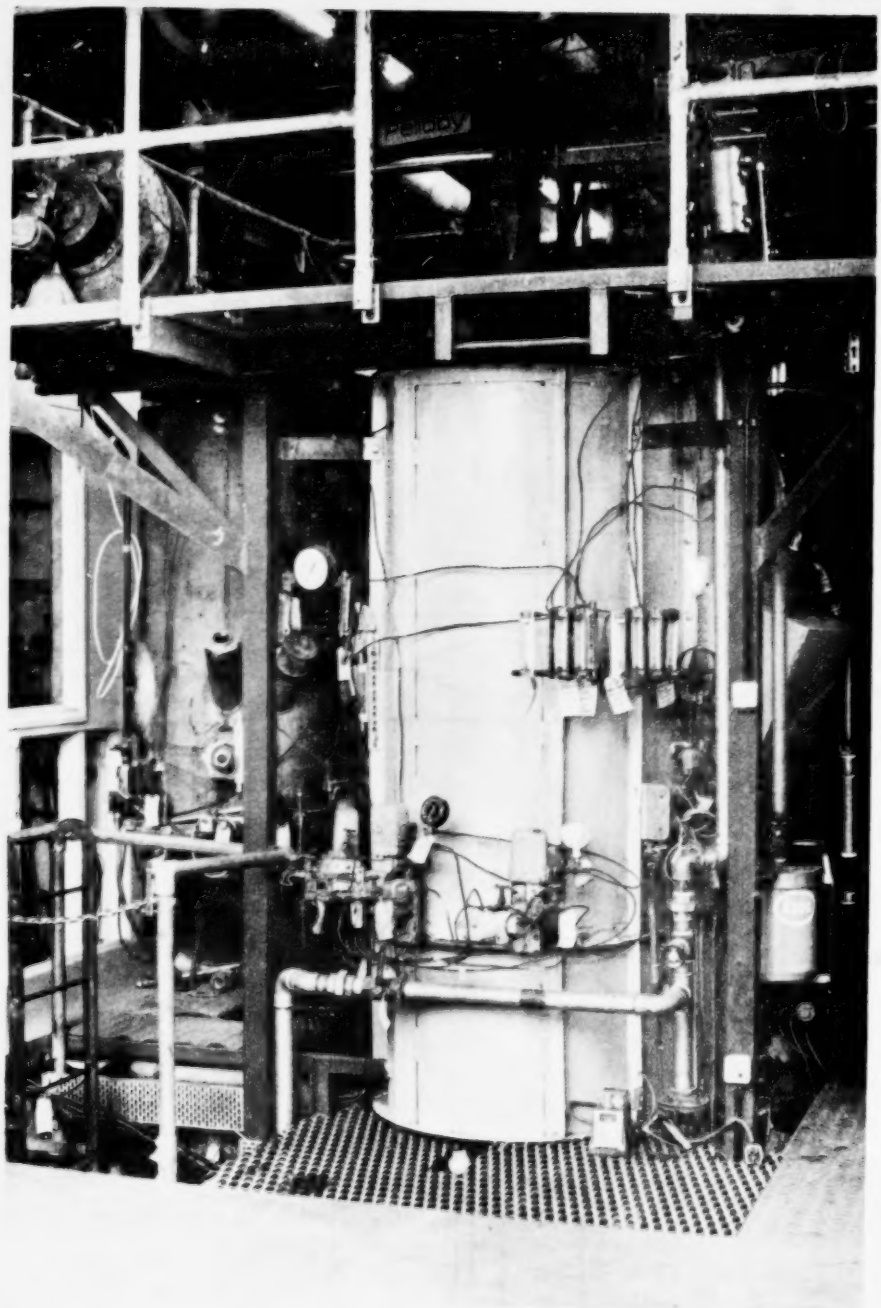

Figure 4. The Esso England continuous CAFB pilot plant.

environmental impact of the combustion of these fuels, sulfur-in-fuel regulations were adopted. In Japan, for instance, utilities are required to burn fuels with as low as 0.1 percent sulfur by weight to no greater than about 1.0 percent sulfur. One method of producing these low sulfur fuel oils (LSFO) is direct HDS of reduced atmospheric crudes.

Since 1968, reduced crude direct HDS technology has been applied to product LSFO from Middle East atmospheric residues. There are at this time 11 commercial direct HDS units operating with a combined production capacity of 459,000 barrels (73×10^3 m^3) per day of LSFO. Ten of the 11 units are in Japan.

The direct HDS process consists of seven interconnected unit operations:

1. Storage and Pretreatment.
2. Reaction.
3. Separation.
4. Recycle Gas Purification.
5. Sulfur Recovery.
6. Tail Gas Treatment.
7. Fractionation.

Atmospheric reduced crude from the storage and pretreatment section passes into the reactor after being combined with makeup hydrogen and recycle gas. In the reactor, the sulfur in the reduced crude combines with the hydrogen to form hydrogen sulfide (H_2S). The reactor effluent

enters a series of flash vessels which separate the stream into liquid, recycle-gas, and sour fuel gas fractions. The liquid streams pass to a distillation column for fractionation into LSFO, middle distillate, naphtha, and sour fuel gas. The recycle gas goes to an amine scrubber where the H_2S is removed. (It is necessary to remove the H_2S, since its presence in the hydrogen-rich recycle gas would reduce the desulfurization rate.) This purified recycle gas is either used as quench gas to moderate the reactor's temperature or mixed with the feed and makeup hydrogen. The rich amine passes to an amine regenerator for separation of the recycle amine and H_2S.

The H_2S rich off-gas stream from the amine regenerator passes to a Claus unit for recovery of the sulfur. The Claus feed stream may contain 95-99 percent H_2S, of which about 97 percent is converted into molten sulfur. The unconverted H_2S exits the unit in the form of SO_2. Since the SO_2 concentrations in the Claus tail-gas are generally significantly higher than national or local standards, additional control, in the form of a tail-gas treater (TGT), is required.

2.3.7 Upgrading of Residual Oil Followed by HDS and Conventional Combustion

This category of residual oil usage involves the upgrading of residual oil and then using HDS followed by conventional combustion. The upgrading can be a simple demetallization which uses techniques and catalysts like those used for HDS. Another upgrading technique involves Flexicoking(R)

which is de-asphalting or coking followed by HDS. In some cases only a vacuum still is used to prepare the feed for the HDS unit. Once the pretreatment has been accomplished, the HDS follows the path outlined in the HDS section above.

2.4 History of the IERL-RTP Program Relating to Residual Oil

The IERL-RTP program for residual oil may be considered in several parts: one part concerned mainly with the CAFB process and its relationship to alternate processes, a second part concerned with the environmental assessment of residual oil usage in general, and a third part dealing with control technology development for the treatment of residual oil.

2.4.1 The CAFB Process and Its Relationship to Alternatives

The CAFB portion of the IERL-RTP program began in June 1970, when a predecessor agency of EPA entered into a joint development program with Esso Petroleum Company, Ltd. Development of the process had begun in 1966, with Dr. Gerald Moss of Esso Research Centre, Abingdon, U.K., and others undertaking experimental work. A patent was issued based on this early work, which was done under the sole sponsorship of Esso Petroleum, Ltd.

The EPA involvement resulted in six separate contracts with Esso Research Centre, Abingdon (ERCA). The work through 1973 is described in a series of reports to the EPA. During this period, a continuous unit (as opposed to the previous batch type units) was commissioned. Runs in

excess of 300 hours were made in this unit using a feedstock of atmospheric distillation bottoms from the Amuay refinery. Ten runs have been completed on the continuous unit and over 3000 hours of operation have been logged.

Subsequent to the findings of the development effort, EPA obtained a technical and predicted cost review which confirmed that the CAFB was viable when compared to the alternatives such as flue gas scrubbing or HDS of heavy residual oil. The review is updated periodically and a current EPA contract, 68-02-2142, with Westinghouse Research Laboratories has, as a part of the effort, current review and update of the CAFB process.

In 1972, a search for a utility partner for a possible demonstration was launched, and in early 1973, a utility agreed to participate in further studies and in the design effort for a demonstration of the atmospheric-pressure CAFB process. A preliminary design and cost estimate for a 50 MWe unit was carried out through cooperation of the EPA contractor, the utility partner, an engineering firm under subcontract, and a sulfur recovery process developer. At the time a decision point was reached, in April 1975, strong pressure was exerted by the U. S. Government to turn all boilers capable of firing coal to this fuel. Since the specific boiler under consideration was capable of firing coal, the conversion from the low sulfur oil then being fired in the boiler to a high sulfur residual oil via the CAFB process was dropped.

In April 1975, a utility and an engineering firm who had been considering the CAFB process on private basis were located. Discussions indicated that agreement could be reached in which EPA would underwrite the design costs

and the utility would underwrite the equipment and fabrication effort. This avoided both the complexity of a three-party contract and the need for the Government to acquire an interest in capital equipment, which would require a complex "buy back" negotiation to protect the interests of the Government.

In June 1975, a letter contract (68-02-2106) was signed by EPA with the engineering firm Foster Wheeler Energy Corporation (FWEC), and the details of a contract between FWEC and the utility (Central Power and Light (CPL) of Corpus Christi, Texas) were negotiated. Design work under the EPA contract began immediately, but the CPL-FWEC contract could not become operative until the arrangements between CPL and other utilities sharing in the effort received the approval of the Securities and Exchange Commission. The final approval was received and the contract made operative in March 1976. Shortly afterwards, the EPA-FWEC contract for the design effort was converted from a letter contract to a standard contract with all clauses and provisions, costs, and other items defined exactly.

Reference was made to supporting contracts for the CAFB demonstration. In mid-April of 1977, a count showed 10 contracts active in direct support of the CAFB demonstration effort. Some of these were relatively limited in both scope and period of performance, such as the contract with GCA of Bedford, Mass., for sampling of the continuous unit and for preliminary environmental assessment of the CAFB process based on the sampling effort and contract reports. Others, such as the contract for the basic effort with FWEC, were much broader in scope, giving rise to subcontracts, and extended for 3 to 4 years.

The EPA program does not aim solely for demonstration of a process, but rather seeks to develop an economically viable process with consideration for the multimedia effects on the environment from the beginning of development. This concern is exemplified by the infrastructure of supporting contracts which are included in the EPA supported CAFB program. All of the contracts contain tasks related to assessing the environmental impacts and to solving any potential adverse environmental impacts which may result from operation of the CAFB process. The availability and handling of heavy residual fuels, the possible means of disposal or sale of spent bed material, the properties of spent bed material after various treatments, the possibility of rejecting all sulfur as calcium sulfate, the applicability of the CAFB as a retrofit, the size of the market, the composition of the market, the locality of probable CAFB usage related to the raw material supply of bed material, the limits of fuel parameters acceptable for CAFB feedstock, the removal and retention of trace and hazardous materials by the CAFB process, and the sulfur removal efficiency are but a few of the areas of the CAFB process considered in the program administered by the Industrial Environmental Research Laboratory at Research Triangle Park, N. C., under EPA's Office of Research and Development.

2.4.2 Environmental Assessment of Residual Oil Usage

The second part of the IERL-RTP residual oil program can be traced from May 1976, when Catalytic, Inc., began environmental and economic assessments of methods utilizing (or capable of utilizing) residual oil to produce electricity. The methods were classified by state of development into one of three categories or phases of work:

Phase I: Processes, such as hydrodesulfurization (HDS), flue gas desulfurization (FGD), and partial oxidation (POX), which are operating or in commercial design.

Phase II: Processes, such as Chemically Active Fluidized Bed (CAFB), which are in the demonstration plant design but have a good chance of becoming commercially feasible during the 3 years of the contract.

Phase III: Processes, such as residual oil solvent extraction (ROSE), which are in the pilot plant phase of development.

The effort during the first year (May 1976-May 1977) was the assessment of the Phase I processes. A Catalytic, Inc. report (see Section 8.2) presents the information obtained, status, conclusions, and recommendations for the three Phase I processes: HDS, FGD, and POX. Preparation of the work plan for the Phase II assessment of CAFB is underway.

Descriptions of the POX, HDS, and FGD processes appear in the report. Since HDS and FGD are commercial and operating, the emphasis for each of these is on the presentation and discussion of information obtained on the units visited.

Catalytic prepared a work plan describing six major task areas. The Catalytic report descusses the work performed and the status of each task.

Based on the information obtained and the progress made, Catalytic drew conclusions as to the environmental information necessary for each process.

2.4.3 Control Technology Development for Residual Oil Treatment

The third part of the program began in the early 1970's and involves two types of investigations. One is a research grant project with Dr. Satterfield at MIT to develop basic data on the interactions between HDS and hydrodenitrogenation (HDN); the other is a development program to obtain better catalysts to promote HDS and HDN.

The research program began with simple model compounds, and looked at the gas phase reactions for the compounds alone and in the presence of each other. As a start, work was conducted at low pressures (less than 12 atmospheres), and temperatures of 200 to 400°C with various commercial catalysts in a flow microreactor. The model compounds were pyridine and thiophene. Results indicated that interactions are affected by changes in temperature caused primarily by a shift in the rate-controlling step. Work continues at high pressures with more complex compounds such as quinoline.

A catalyst/sorbent development program was initiated in 1972, with Hydrocarbon Research, Inc., at Trenton, New Jersey. The initial objectives were to investigate low cost demetallization catalysts at the laboratory level, select and test the most promising, and estimate the cost and viability of using the demetallization step before conventional HDS. These objectives were met with a 1973 publication which indicated the potential for the technique. The low cost demetallization catalyst was

a 20 x 50 mesh activated bauxite, impregnated with small amounts of molybdenum.

The next phase of the work investigated optimizing the amount of molybdenum, exploring commercial technology for producing the catalyst, and testing of the catalyst which was produced using commercial techniques. A 1975 report on this work indicated that the 1 percent molybdenum loading had the best potential, and small-scale pilot plant testing with different difficult-to-desulfurize vacuum residual oils was conducted. These tests indicated that the technique was still viable, but additional tests would be required to determine the tradeoff of metals and sulfur removal in the first step, demetallization, versus their removal in the second step, HDS.

Tests were conducted at various demetallization operating conditions to optimize the overall desulfurization. These were reported in a 1976 publication, and they indicated that the new first stage catalyst, when used in an overall two-stage demetallization/desulfurization process, offers a substantial operating cost advantage over a direct desulfurization process for producing low sulfur fuel oils from high metals petroleum vacuum residua. Work since then has concentrated on the effect of pore size distribution on catalyst activity for HDN.

3. ACCOMPLISHMENT PLANS/SUBOBJECTIVES/WORK TASKS

All work underway on Residual Oil Processing is being done under the Accomplishment Plan for "Energy Control Technology - Fuel Processing." The following Subobjectives and Work Tasks are being pursued:

Subobjective: Environmental Assessment

Work Tasks: Environmental Assessment of Residual Oil Usages

Analytical Support for Residual Oil Usage/ Determination of Hazardous Substances

Subobjective: Chemically Active Fluid Bed Residual Oil Cleanup

Work Tasks: Chemically Active Fluid Bed on Small Commercial Scale

Demonstrate Chemically Active Fluid Bed on Small Commercial Scale

Engineering Support of Chemically Active Fluid Bed Demonstration

Multiple Option Service Contract Tasks in Support of the Fluid Bed Demonstration

Subobjective: Control Technology Development

Work Tasks: HDS/HDN Interactions in Liquid Fuels

Control Technology for HDS/HDN of Liquid Fuels

4. MEANS OF ACCOMPLISHMENT

4.1 Participating Contractors/Grantees

The following listing of all participating contractors and grantees by Work Task includes Project Officer, Contract Number, start date, and contract period:

- "Environmental Assessment of Residual Oil Usages," Catalytic, Inc., S. L. Rakes, Contract No. 68-02-2155, started 5-11-76, to run for 36 months.

- "Analytical Support for Residual Oil Usage/Determination of Hazardous Substances," Westinghouse R&D Center, S. L. Rakes, Contract No. 68-02-2638, started 5-12-77, to run for 24 months.

- "Chemically Active Fluid Bed Development and Support," Esso England, S. L. Rakes, Contract No. 68-02-2159, started 5-6-76, to run for 36 months.

- "Residual Oil Disposition Status Report," A. D. Little, S. L. Rakes, Contract No. 68-02-1332, Task 19. Started 8-21-75, ended 4/76.

- "Demonstrate Chemically Active Fluid Bed on Small Commercial Scale," Foster Wheeler, S. L. Rakes, Contract No. 68-02-2106, started 6-17-75, to run for 55 months.

- "Engineering Support of Chemically Active Fluid Bed Demonstration," Westinghouse R&D Center, S. L. Rakes, Contract No. 68-02-2142, started 2-16-76, to run for 30 months.

- "Multiple Option Service Contract Tasks in Support of Fluid Bed Demonstration," GCA Corporation, S. L. Rakes, Contract No. 68-02-2632, started 1-21-77, to run for 12 months.

- "HDS/HDN Interactions in Liquid Fuels," MIT, T. W. Petrie, Grant No. R804123, started 8-1-75, to run for 36 months.

- "Control Technology for HDS/HDN of Liquid Fuels," Hydrocarbon Research, Inc., T. W. Petrie, Contract No. 68-02-0293, started 12-13-72, to run for 55 months.

- "Environmental Assessment of Residues from the FBC of Coal and the Gasification of High-Sulfur Fuel Oils," Ralph M. Stone and Co., S. L. Rakes, Contract No. 68-03-2347, started 12-5-75, to run for 48 months.

4.2 Scope of Work Outlines and Descriptions of Active Projects

- Environmental Assessment with Systems Analysis and Program Support for Residual Oil Usage. Catalytic, Charlotte, N. C., Contract No. 68-02-2155.

  A. This will be a continuing, broad, and comprehensive environmental and engineering analysis, with source sampling and ambient monitoring.

  B. Contractor Tasks.

     1. Review of existing environmental, engineering and cost data.

2. Identification of important pollutants and projection of attainable emission levels.

3. Identification of missing information and design of program to develop this information.

4. Design and execution of source sampling, fugitive emission, and ambient measurement program.

5. Provide general program support.

   a. Literature searches.

   b. Information storage and retrieval.

   c. Assessment of related R&D

   d. Technical review and evaluation.

   e. Others as required.

- Analytical Support, Hazardous Substances. Westinghouse Research Laboratories, Contract No. 68-02-2638.

A. An analytical support effort to determine what substances are present in residual oil which could become environmental pollutants. This work is coordinated with the work being done by the Process Measurements Branch (PMB) of IERL-RTP. The Health Effects Research Lab (HERL) also has input to this effort.

B. Contractor Tasks.

1. Survey of currently available data.

2. Survey and classification of residua.

3. Selection of samples and test plan.

4. Sample acquisition.

5. Analysis of samples (including bioassay).

6. Recommendations for use of the various residua.

- Preliminary Environmental Assessment of the CAFB Process. GCA, MOSC Task 14, Contract No. 68-02-1316.

  A. A MOSC Task (3000 hours) to sample the CAFB pilot unit and to lay the groundwork for Environmental Assessment of the process.

  B. Contractor Tasks.

     1. Analyze, in depth, the potential multimedia environmental impact of the CAFB process.
     2. Determine the tests which should be run on the Esso Petroleum Pilot Plant to comprehensively evaluate the existence of various pollutants.
     3. Evaluate the tests made.
     4. Analyze the gas absorption, particulate, and generator bed material samples.
     5. Compare the CAFB process with other gasification schemes.
     6. Perform ESCA (Electron Spectroscopy for Chemical Analysis) on selected samples.
     7. Make recommendations for the sampling plan to be followed for the CAFB demonstration.
     8. Prepare a report with recommendations on followup for: (1) the Esso Petroleum project; (2) CAFB Demo test program; (3) the full Environmental Assessment project.

- Residual Oil Disposition Status Report. A. D. Little, MOSC Task 19, Contract No. 68-02-1332.

  A. A MOSC Task (1000 hours) to provide input for the planning of the residual oil program and to assess the probable extent and trends of the use of residual oil.

B. Contractor Tasks.

1. Determine the approximate supply of residual oil in the U. S. available for fuel use, now and in the future.
2. Determine the distribution of this residual oil supply.
3. Determine the present usage of residual oil.
4. Project how the supply and demand might be modified if an environmentally sound use of residual oil as a fuel were available.

- Study of Chemically Active Fluid Bed Process (CAFB) for Sulfur Removal During Gasification of Heavy Fuel Oil. Esso Petroleum Company, Esso Research Centre, Abingdon (ERCA), Contract No. 68-02-1359.

A. This contract covers phase III of a six-phase program conceived for the development of the CAFB process. The purpose is to provide design information to permit a conceptual design for a conversion of a utility boiler to the CAFB process.

B. Contractor Tasks.

1. Test three sorbent stones (U.S. limestones) and two fuel oils in the batch units to measure reactivity and dust formation.
2. Derive a useful engineering design guide to the process from data gathered in phases I and II.
3. Modify the continuous unit and test a U.S. stone and oil (Run 8).
4. Run the continuous unit to provide design data and/or

test alternative limestone (Run 9).

5. Provide advice and consultation to other EPA contractors working on the CAFB effort.
6. Test materials of construction.
7. Determine trace metals retention by the sorbent bed material.
8. Determine the feasibility of burner design modification to permit on-stream decoking of the gas duct.
9. Evaluate alternate low cost methods for purge stone and regenerator off-gas disposal.

° Studies of the CAFB Gasification Process for Reduction of Sulfur Oxide Emissions. ERCA, Contract No. 68-02-1479.

A. This is a follow-on contract to -1359 to allow uninterrupted development of the CAFB process with emphasis on acquiring design information and providing support for the design of a U. S. demonstration. This contract begins phase IV of the six-phase effort outlined for the CAFB process development.

B. Contractor Tasks.

1. Test a new fuel and three new limestones in the batch units.
2. Analyze data from previous tests, predict performance of continuous unit.
3. Test proposed design features of demonstration unit in the continuous unit (Run 10).
4. Evaluate, in a continuous unit run, up to six items related to the planned demonstration (Run 11).

5. Provide advice, consultation, and technical expertise to support the design of the demonstration unit.

6. Determine effect of CAFB process on potentially harmful elements, including sulfates and free acids, other than SO_2 and NO_x.

- Environmental Assessment and Development of CAFB Process for Evaluation of a Clean Fuel Gas in an Existing (or New) Combustor. ERCA, Contract No. 68-02-2115.

  A. This contract is to make available, to the CAFB demonstration design effort, Esso-generated data on the potential for employing the CAFB process on solid fuels.

  B. Contractor Tasks.

     1. Abstract data and conclusions from Esso proprietary reports on laboratory studies made for gasification of a number of coals and lignites; prepare a formal report to EPA.

     2. Evaluate the Esso continuous unit for use in test of various gas cleanup schemes.

     3. Make maximum use of proprietary studies, produce a conceptual design for a pressurized CAFB process, and compare to alternative clean power generation systems.

- Technical Support for the CAFB Demonstration. ERCA, Contract No. 68-02-2159.

  A. This contract will cover phases V and VI of the planned six-phase CAFB development program, and provide the

necessary support by ERCA to the CAFB demonstration.

B. Contractor Tasks.

1. Provide coal feed and steam supply to the continuous unit. Add data logging equipment, and test design and operating parameters concurrent with Run 11.
2. Modify continuous unit to include design features of the demonstration unit and test in continuous Run 12 under long-day operating conditions.
3. Modify continuous unit and operate (Run 13) to provide problem solution for verification of the demonstration shakedown and commissioning activities.
4. Provide input for and attend design review meetings conducted during the demonstration project.
5. Conduct batch unit tests on three solid fuels and two bed materials selected for the demonstration unit.
6. Investigate and recommend a solution for dealing with the coal ash in the CAFB unit.
7. Refine previous data analyses and develop a predictive mathematical model for the CAFB process.
8. Provide information needed, and help prepare, an operations manual for the demonstration unit.
9. Assist in the commissioning of the demonstration plant and provide assistance at key points in the experimental program.

- Demonstration of the Chemically Active Fluid Bed (CAFB) Process on a Small Commercial Scale. Foster Wheeler Energy Corporation (FWEC),

Contract No. 68-02-2106.

A. This contract is to develop a definitive process design for a CAFB process to feed two burners of the No. 4 unit at La Palma Station of the Central Power and Light Company (CPL) at San Benito, TX. The overall objective of the program is to demonstrate the effectiveness and practicality of the CAFB process to provide fuel from feedstock not environmentally acceptable if fired directly. Fabrication of vessels, construction of the units, etc. are covered under a private contract between CPL and FWEC.

B. Contractor Tasks.

1. Design preparation and review.
   a. Design development.
   b. Fuel selection.
   c. Definitive design.
   d. Process design manual.
2. Construction planning.
   a. Site planning and approval.
   b. Construction and fabrication drawings.
   c. Monitor construction progress.
3. Experimental test program.
   a. Operating variables (primary liquid fuel).
   b. Daily inspections.
   c. Emission measurements.
   d. Emission correlations.
   e. Spent materials studies.

4. Performance and emission testing.

   a. Records of power, maintenance supplies, etc.

   b. Daily inspections.

   c. Emission measurements.

   d. Emission correlations.

   e. Spent materials studies.

5. System evaluation.

   a. Process design manual update.

   b. Conceptual design of commercial system.

° Evaluation of the Fluidized Bed Combustion Process, Fluidized Bed Residual Oil Gasification/Desulfurization Demonstration. Westinghouse Research Laboratories, Contract No. 68-02-0605.

A. A contract designed to provide engineering and program support for the CAFB program. Only modification 6, to the basic contract, is concerned with CAFB and active at this time.

B. Contractor Tasks.

1. Sulfur removal system.

   a. Sorbent selection.

   b. Spent sorbent processing.

   c. Spent sorbent utilization.

   d. Environmental impact of spent sorbent disposal.

   e. Sulfur recovery.

2. Solids transport testing.

3. Boiler gasifier interfaces.

4. Pilot plant test program support.

5. Process design cost and evaluation.

6. Market studies.

   a. Fuel.

   b. Limestone.

   c. Applications.

   d. Competitive technology.

- Engineering Support of the CAFB Demonstration. Westinghouse Research Laboratories, Contract No. 68-02-2142.

A. This contract is a follow-on to -0605 and is designed to provide engineering and program support for the CAFB demonstration.

The engineering and laboratory scale regenerative work under this contract is meshed with the CAFB demonstration in Texas, while the work under -0605 was general, or was meshed with a once-through CAFB demonstration that was contemplated in New England.

B. Contractor Tasks.

1. Sulfur removal system.

   a. Sorbent screening and selection.

   b. Sorbent disposal.

   c. Environmental impact.

   d. Sulfur recovery.

2. Alternative concepts.
    a. Sorbents.
    b. Fuels.
    c. Applications.
    d. Catalysts in regenerator.
    e. Process.
    f. Design and operating concepts.

3. Environmental control technology.
    a. Waste gas cleaning.
    b. Waste water control.
    c. Waste solids treatment.
4. Environmental impact for off-design conditions.
    a. Startup.
    b. Shutdown.
    c. Burnout.
    d. Equipment malfunction.
    e. Emergency conditions.
5. System evaluation.
    a. Plant emission control.
    b. Capital and operating costs.
    c. Reliability.
6. Program assistance.
    a. Data evaluation.
    b. Critical design features and experiments.
    c. Market potential.
    d. Related technology.

- Development of Sampling and Analytical Techniques.

  A. Studies are being done in-house by the Process Measurements Branch (PMB) to include close liaison with contractors who are performing sampling and analytical work.

- Environmental Assessment of Residues from the Fluidized Bed Combustion of Coal and the Gasification of High-Sulfur Fuel Oils. Ralph M. Stone and Co., Contract No. 68-03-2347.

  A. This contract is administered by the EPA's Environmental Research Laboratory (Cincinnati) with funding from both the FBC and CAFB sector of the Industrial Environmental Research Laboratory (Research Triangle Park). The objective is to determine the environmental impact of solid waste from the CAFB process.

  B. Contractor Tasks.

     1. Residue and preliminary leachate characterization.
     2. Literature review of environmental impact of like substances.
     3. Environmental impact -- laboratory studies using columns to simulate terrestrial disposal.
     4. Market study -- possible sale for manufacturing use.
     5. Residue treatment and disposal study.

- Catalytic Desulfurization and Denitrogenation Interactions. MIT, Grant R804123.

  A. This is a continuing research effort to determine the characteristics and kinetics of simultaneous HDS/HDN reactions in

order to develop improved methods of converting organo-nitrogen compounds to innocuous products.

B. Grantee Tasks.

1. Conduct experimental studies of HDN and HDS at pressures representative of industrial practice.
2. Use model compounds typical of more complex sulfur and nitrogen compounds (multi-ring compounds).
3. Determine thermodynamic limits on steps in denitrogenation pathways.
4. Formulate interactive kinetics of HDS/HDN, including effects of H_2S and NH_3.
5. Determine the effects of catalyst variations (e.g., activity) on the reactions.

- Demetallization of Heavy Residual Oils and Denitrogenation Catalyst Evaluation. Hydrocarbon Research, Inc., Contract No. 68-02-0293.

A. This effort has two main thrusts. The first is to develop and evaluate scavenger pretreatment systems for high-metals, high-sulfur residual oils, and the second is to evaluate catalyst characteristics for removal of nitrogen from liquid fuels.

B. Contractor Tasks.

1. Survey to determine types of compounds and supports that might be suitable for demetallization.
2. Evaluate selected combinations via screening runs.
3. Optimize the promoter/scavenger catalyst and

evaluate a commercial production of the catalyst.

4. Optimize the run conditions for the pretreatment using the developed catalyst and different residual oils.
5. Evaluate similar technology in the USSR for pretreatment.
6. Evaluate catalyst characteristics for denitrogenation of liquid fuels.

5. CURRENT STATUS: ENVIRONMENTAL ASSESSMENT

5.1 Progress

5.1.1 General

The environmental assessment tasks included in the Control Technology contracts have progressed well. Esso Petroleum has studied trace metal retentions by the bed material and disposal and weathering of treated bed material. Experimental effort by Esso in the dry sulfation technique was not promising. Westinghouse achieved some very promising results on small scale Thermal Gravimetric Analysis (TGA) and theoretical studies of this dry sulfation technique. The GCA effort in performing sampling and in preliminary Environmental Assessment of the CAFB process, including projection of results at the Texas demonstration site, was well received; and indicates favorable results for the CAFB process. The Catalytic effort has classified residual oil usage techniques into five categories and has begun detailed assessment of each process category. Many data have been gathered which will be anlayzed, and then plans will be made to fill the data gaps.

5.1.2 Project by Project

Much Environmental Assessment work is included in the Control Technology Development contracts for the Chemically Active Fluid Bed Process. The Esso Petroleum Ltd. effort includes determination of the retention by the bed of trace and potentially hazardous materials. Significant retention by the bed material of vanadium, nickel, sodium and other trace minerals was shown by spark source mass spectrometry. Neutron Activation analysis was used on some samples for a comparison analysis. Mass balances

were computed for beryllium, cadmium, antimony, molybdenum, nickel, vanadium, tellurium, arsenic, selenium, chromium, manganese, cobalt, boron, lead, sodium, and potassium. Significant retention of many of the elements was indicated.

Another environmental assessment effort by Esso Petroleum investigated the disposal of spent bed material via two routes: first, deadburning; second, the "dry sulfation" technique. Material which had been deadburned under several conditions and untreated bed material were exposed to outside weathering for 1 year. Temperature rises were monitored and tests of leachate water and of the bed material were conducted periodically. The results were compared to World Health Organization standards for potable water. Various trials and tests were conducted of the dry sulfation technique, in which spent bed material is converted to calcium sulfate ($CaSO_4$), and SO_2 from the regeneration step is captured.

The results of the Esso Petroleum effort are given in report EPA-600/2-76-248, September 1976. In summary, the dry sulfation approach does not appear commercially attractive, while deadburning produces a product that seems easily disposable.

The Westinghouse Research Laboratories engineering analysis/support contract includes detailed sorbent disposal and usage studies. Westinghouse has performed small scale tests and paper studies on the dry sulfation step for disposal. They believe that it may be made into a viable process, especially since this option eliminates a sulfur recovery plant when setting up a CAFB process unit. The use of spent bed material by the building industry as aggregate, and perhaps as a constituent of mortar and cement, is possible. Two markets identified for bed materials which

are under exploration by other groups are agricultural use and use in sewage treatment. Various concrete mixtures have been tested by Westinghouse using spent bed material and fly ash. The Belgian Trief process is being closely investigated by Westinghouse: this process uses spent bed material as a substitute for Portland cement in concrete.

The environmental impact of land disposal is a task that Westinghouse has investigated using leaching tests, photomicrographs, scanning electron microscopy, and other techniques. Methods, parameters, and leachate characteristics have been identified. The summary trace element results are compared to drinking water standards. In all cases the trace elements in the leachate were within drinking water standards. The permissible calcium level was exceeded, but it was noted that calcium in leachate from natural gypsum deposits also exceeds drinking water standards.

Ocean dumping is not considered a likely solution to spent sorbent disposal; however, use of the material to build artificial reefs for improved fish habitat is being considered.

The Foster Wheeler contract for demonstration of the CAFB process includes effort on the determination of the disposal characteristics of the spent bed material. This is largely covered in a subcontract from Foster Wheeler to Battelle Columbus Laboratories. Other EA effort planned for FWEC calls for trace element analysis on bed material and effluents and emissions tests per NSPS requirements. This work is not now active. The baseline testing of the boiler, as found before the CAFB retrofit, is complete.

One preliminary environmental assessment task was completed under a multioption services contract (MOSC) by the GCA Corporation. This task included sampling the Esso Petroleum continuous pilot unit while using residual oil and bitumen as a feedstock, and making a preliminary environmental assessment of the process with projections of emissions from those of the Esso pilot to those of the demonstration unit in Texas. The analytical techniques used included ESCA (electron spectroscopy for chemical analysis), mass spectrometry, and chromatographic techniques. The probable environmental impact of the unit in Texas was judged acceptable. The one possible area of concern was in particulate emissions. This effort is reported in detail, with the necessary background information, in report EPA-600/7-76-017, "Preliminary Environmental Assessment of the CAFB."

Another MOSC task in the EA area was that on Residual Oil Supply and Usage in the U.S., with consideration of environmental consequences, which Arthur D. Little performed. This effort projected the residual fuel supply and demand to 1985 and indicated areas of concern. This work is reported in EPA-600/2-76-166, "Residum and Residual Fuel Oil Supply and Demand in the U.S. 1973-1985."

The major environmental assessment contract for residual oil usage is held by Catalytic, Charlotte, North Carolina. This contract was effective in May 1976.

The objective of this work is to execute an environmental assessment from a system analysis of the present commercially operating processes

capable of using residual fuel oil to generate electricity. The processes under study include:

1. Pretreatment - Hydrodesulfurization (HDS) processing removes sulfur and other pollutants from fuel oil prior to combustion.
2. Conversion - Partial oxidation (POX) and chemically active fluidized bed (CAFB) processing convert residual fuel to an environmentally acceptable gas, which can be used directly or in a combined cycle system.
3. Post-treatment - flue gas desulfurization (FGD) techniques remove pollutants by cleaning the tail-gas from conventional boiler combustion.

To date, all existing data have been compiled on residual fuel oil processes. An intensive study of three major processes was required for the assessment of present commercial technology. The information obtained on the processes was reviewed for a detailed engineering and cost analysis. At the present time, several economic studies are being conducted for commercial POX schemes. Five FGD systems and four HDS processes have been reviewed. A study of combined cycle units is underway. The commercial status of the processes under study shows that there are numerous units now in operation having significant capacities and operating experience.

Residual fuel oil contains hydrocarbons and certain contaminants such as sulfur, ash, and metal. These contaminants can be potential pollution problems as they are transferred to various forms in the different processes. Sulfur data are well defined on all H_2S and SO_2

removal processes.

Very little data are available on other potential pollutants including vanadium, nickel, NO_x, ash, particulates, and carcinogenic compounds. All important emission levels from the process units have been calculated; however, it will be necessary to analyze samples from various cleanup processes in order to determine present and future emission levels. No problems are anticipated with excess pollution from sulfur in the effluent gas from these processes.

Investment costs and operating requirements have been used to estimate the control costs and efficiencies. Data collected on a trip to Japan were helpful in making these estimates and in obtaining missing information on commercial HDS, POX, and FGD processes. Some missing information still exists in the area of treatment and final disposal of some effluent streams, which contain important pollutants such as metals, carbon, and ash compounds. Further plant visits will be required to obtain samples of these streams. Samples from plants will be analyzed to determine the potential pollution products. The necessity of a sampling program for each process will be considered. Calculations within an order of magnitude would perhaps suffice in some cases; however, emission data are required through sampling to complete the environmental assessment.

It is concluded that each process under study is established as an acceptable unit by operating experience on a commercial scale. The flexibility of each process has been demonstrated by a proven acceptance of variable feedstocks within certain design limits. Contaminants such as

sulfur, nickel, and vanadium are successfully removed from the fuel. In some cases, they may be used for the production of salable by-products. Additional process equipment is required in most cases to upgrade by-products to a final form. At least 80 to 90 percent removal efficiencies have been demonstrated for most contaminants. Sulfur removal efficiencies of 96 to 99 percent are common in FGD processes.

The capital and operating cost estimates indicate that the price for these processes is high for the U.S.A. The process cost is very sensitive to feed composition. It should become more economical in the future to charge heavier lower-priced feeds into the POX process, middle-range feeds into the HDS process, and low sulfur fuel oils into FGD units.

5.2 Plans

One environmental assessment contract for Analytical Support/ Hazardous Substances in Residual Oil has just been awarded to Westinghouse Research Laboratories. This effort will analyze, in great detail, 100 samples of residual oil. This analysis will include bioassy and radio-nuclide assay as well as detailed organic and trace element analysis.

The GCA Corporation has been awarded a contract to sample the Esso CAFB unit using coal and lignite as a feed, and to compare these results to those found in the earlier effort where oil and bitumen were the feedstocks. The results will be projected to the demonstration unit, and the Preliminary Assessment will be updated.

Milestone charts for each of the two existing EA contracts follow. The work plan for a Westinghouse contract, is currently under development.

1. GCA -- Preliminary EA of CAFB -- Coal and Lignite

Complete Field Testing	October 1977
Complete Engineering Analysis	January 1978
Submit Draft Final Report	March 1978

2. Catalytic, Charlotte -- EA of Residual Oil Usage
(See Figure 5.)

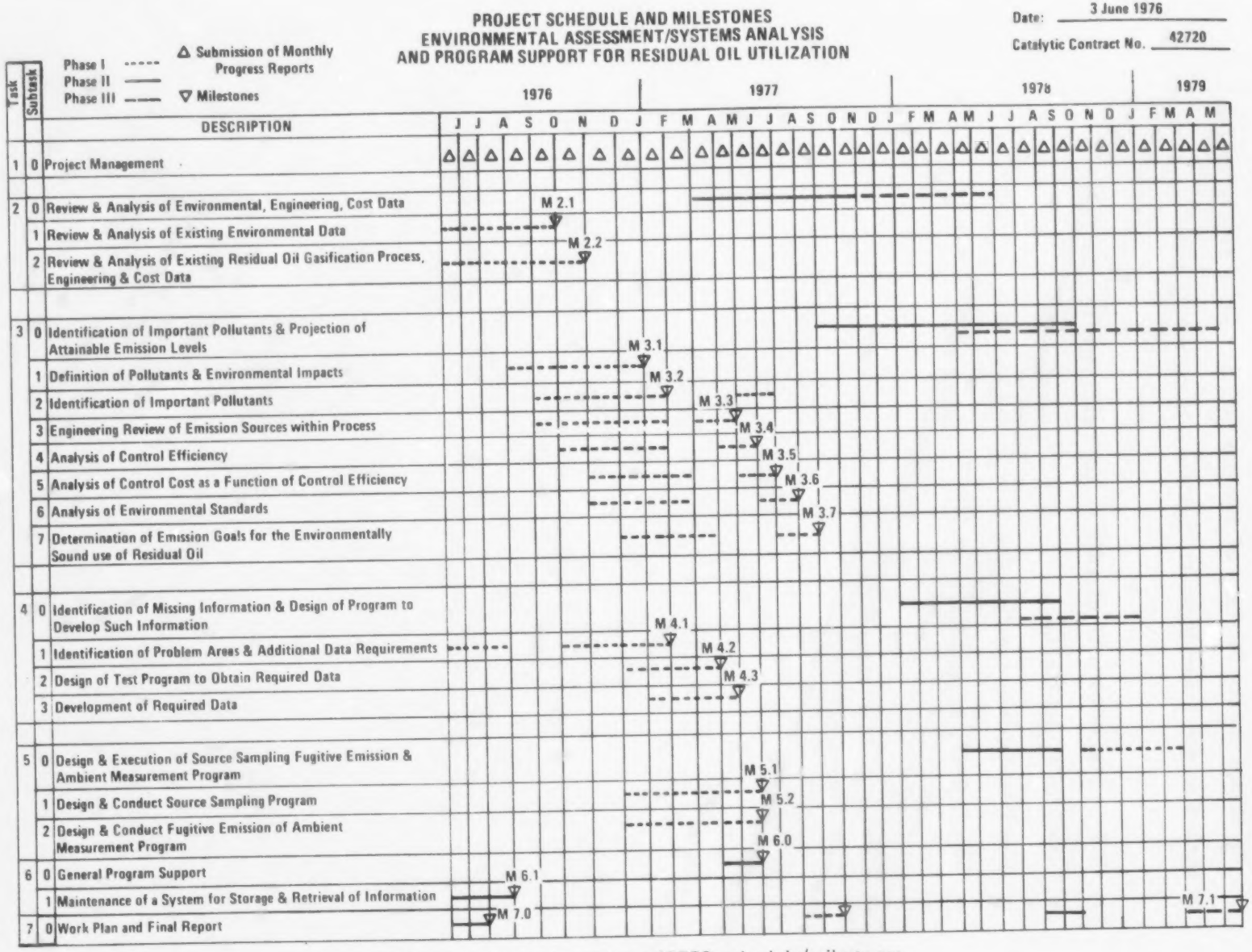
PROJECT SCHEDULE AND MILESTONES
ENVIRONMENTAL ASSESSMENT/SYSTEMS ANALYSIS
AND PROGRAM SUPPORT FOR RESIDUAL OIL UTILIZATION
Date: 3 June 1976
Catalytic Contract No. 42720
Phase I
Phase II
Phase III
Submission of Monthly Progress Reports
Milestones
Task
Subtask
DESCRIPTION
1976
1977
1978
1979
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M
1 0 Project Management
2 0 Review & Analysis of Environmental, Engineering, Cost Data
1 Review & Analysis of Existing Environmental Data
2 Review & Analysis of Existing Residual Oil Gasification Process, Engineering & Cost Data
3 0 Identification of Important Pollutants & Projection of Attainable Emission Levels
1 Definition of Pollutants & Environmental Impacts
2 Identification of Important Pollutants
3 Engineering Review of Emission Sources within Process
4 Analysis of Control Efficiency
5 Analysis of Control Cost as a Function of Control Efficiency
6 Analysis of Environmental Standards
7 Determination of Emission Goals for the Environmentally Sound use of Residual Oil
4 0 Identification of Missing Information & Design of Program to Develop Such Information
1 Identification of Problem Areas & Additional Data Requirements
2 Design of Test Program to Obtain Required Data
3 Development of Required Data
5 0 Design & Execution of Source Sampling Fugitive Emission & Ambient Measurement Program
1 Design & Conduct Source Sampling Program
2 Design & Conduct Fugitive Emission of Ambient Measurement Program
6 0 General Program Support
1 Maintenance of a System for Storage & Retrieval of Information
7 0 Work Plan and Final Report
M 2.1
M 2.2
M 3.1
M 3.2
M 3.3
M 3.4
M 3.5
M 3.6
M 3.7
M 4.1
M 4.2
M 4.3
M 5.1
M 5.2
M 6.0
M 6.1
M 7.0
M 7.1

Figure 5. Catalytic contract 42720, schedule/milestones.

6. CURRENT STATUS: CAFB

6.1 Progress

6.1.1 General

The Chemically Active Fluid Bed (CAFB) program of IERL-RTP has defined the operation of the CAFB using residual oils as a feedstock. The CAFB process has been found to effectively desulfurize the residual oil feedstocks and to give stable process operating conditions. Moderate stone make-up rates of 1.0 to 1.5 moles of calcium to 1 mole of sulfur in the feedstock were found to give sulfur removal effeciencies of 80 percent or more. The ease of control and the efficiency of the process indicated that commercial application was likely. Trials of various solid fuels in batch units, conducted under private sponsorship, indicated that these feedstocks were also feasible for the CAFB process.

The design of the small semi-commercial demonstration unit has been completed, except for minor design changes and field retrofit adjustments found necessary during the construction which began in May 1977. The equipment fabrication and construction of the unit is being done under a contract between Central Power & Light (CPL) and Foster Wheeler (FWEC). CPL is funding the equipment fabrication and the construction of the unit. Figure 6 is a photograph of the CAFB demonstration model.

A contract, for further development of the CAFB process and for technical support of the demonstration effort, was definitized with Esso Petroleum, Ltd. Other contracts for support of the CAFB demonstration were arranged. Ancillary arrangements and subcontracts for fuel, stone, materials handling, etc. are either awarded or are in the advanced review stage.

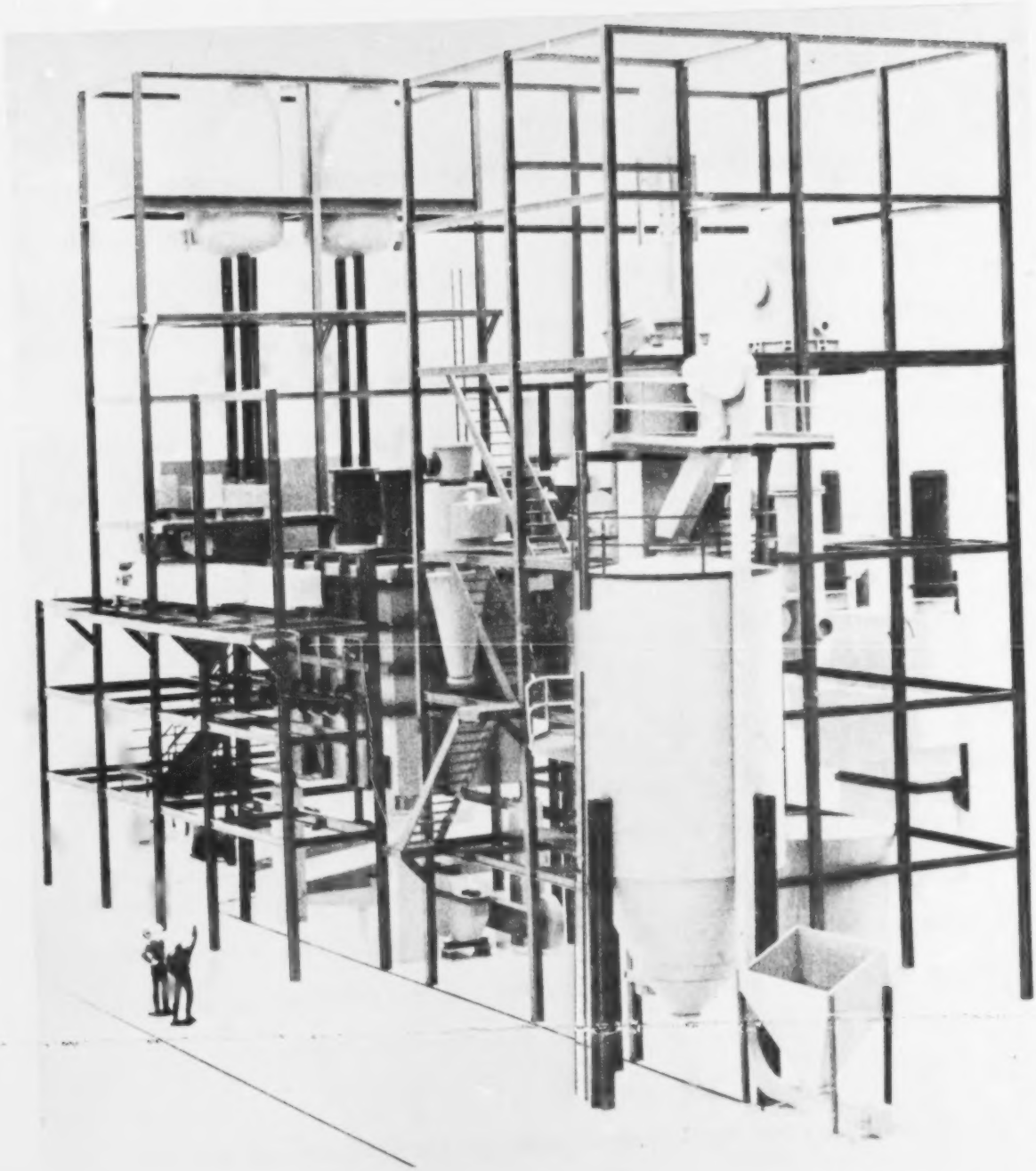

Figure 6. Model of CAFB demonstration unit under construction by CPL at San Benito.

6.1.2 Project by Project

CAFB Demonstration Unit--Foster Wheeler Energy Corp. (FWEC)

Task 1, design preparation and review, is complete except for review meetings, which will be held periodically throughout the period of performance of the contract. FWEC has nearly completed the construction and fabrication drawings. A model, on a scale of 1 to 32, was constructed of the CAFB demonstration unit. Photographs of this model serve the same purpose as isometric drawings of the unit. The model is now being used in construction planning and will be used in operator training. FWEC is monitoring the construction effort and providing periodic briefings to EPA on the progress.

The performance and emission testing planning is nearing completion. The boiler unit has been tested in its original condition. Analysis of the power produced, fuel consumed, and operating conditions is underway.

The theoretical failure analysis portion of Task 5 system evaluation was completed in 1977, and will be updated in 1978 as design changes are made. The remainder of Task 5 deals with the process design manual update and the conceptual design of a larger commercial system. Work will be started after the experimental test program is completed and the information generated by the tests is analyzed.

The remaining two areas of the FWEC contract, Task 6 (reports of work) and Task 7 (management), are on schedule and no significant problems have been found.

CAFB Development and Technical Support of Demonstration--Esso Petroleum

Esso has operated the continuous unit pilot plant to perform preliminary testing of coals, stones, and equipment features to be used in the demonstration plant. "Long-day" operation, that is, startup in the morning, shutdown at night, and startup the next morning, has been demonstrated. Checkout of the data logging equipment is near completion. The scanning and display programs are operational. The pressures, temperatures, and gas analyses are displayed. Several short runs on the continuous unit used a minus 12 mm lignite sizing. Esso demonstrated that, by increasing the pressure drop across the cyclones from the range of 0.25 - 0.5 kPa to the range of 1 - 2 kPa, the efficiency is improved markedly and particulate carryover to the burner is decreased.

Esso completed compilation of a CAFB operating manual, except for sections on data logging and coal feeding. These sections will be completed after Esso has operated the two systems and acquired the experience necessary to write the sections.

Adequate lignite to test the primary solid feedstock for the Texas demonstration in the Esso pilot unit is on hand in England. Some Texas limestone may need to be procured and sent to England at a future date.

Esso has also conducted trace metal determinations on both the incoming feed and the sorbent bed to determine the retention of various elements by the bed material. The retention of these trace metals prevents them from entering the environment where they may inflict ecological damage. Retention also prevents them from causing damage to the boiler via corrosion and fouling.

A conceptual study of the CAFB process, operated at a pressure of about 1.8 MPa, has been completed by Esso Research Center Abingdon and Exxon R&E, Florham Park. This form of the CAFB process is very attractive for use in conjuction with turbines and combined cycle applications.

Based on experience of 10 runs totaling 3,000 hours on the continuous unit, Esso is developing a mathematical model of the CAFB process to be used as a predictive tool in the design and operation of larger CAFB units.

Engineering Analyses and Support of the CAFB Demonstration -- Westinghouse Research

Westinghouse tested several stones for use at the CAFB demonstration site; stones were tested for sulfur removal and attrition. Morphological studies were made in an effort to relate grain size and type of grain structure to stone properties. Both optical and electron microscopes were used in the studies. Stone attrition appears greatest in nearly pure stones with large calcite type grain structure. Various types of stone attrition are being studied; e.g., during initial heating and calcination, fluidization, transport between areas of the CAFB unit, and regeneration.

Westinghouse has investigated spent sorbent processing, spent sorbent utilization, and spent sorbent disposal/environment impact. Their purposes were to determine the properties of spent sorbent, to identify process alternatives, and to identify and solve problems likely to be encountered when dealing with the spent sorbent. Alternate concepts for the CAFB

process -- including alternates to the limestone sorbents, other fuels, applications other than utility usage, and alternate subsystems for regeneration, sulfur recovery, and solids transport -- have been explored under this contract.

Other control technology evaluation for subsets of the unit operations making up the CAFB process -- such as waste gas cleaning, trace element retention, and waste water control -- is being explored as part of the engineering support for the CAFB demonstration.

6.2 Plans

6.2.1 CAFB Demonstration (Foster Wheeler)

The largest remaining effort under the EPA contract is the procurement and delivery of fuels and feedstocks to the demonstration site and testing of the unit for performance and criteria pollutant emissions. Other than the EPA work, the major remaining effort is the construction, check out, and operation of the unit. This is the subject of a contract between FWEC and CPL.

The schedules for both the EPA funded effort and the CPL/FWEC effort are reflected in the Figure 7 milestone chart. The final report will also include a conceptual design for a much larger CAFB unit. This will draw on the data generated by, and the lessons learned during, operation of the La Palma unit and further operation of the Esso pilot plant in England.

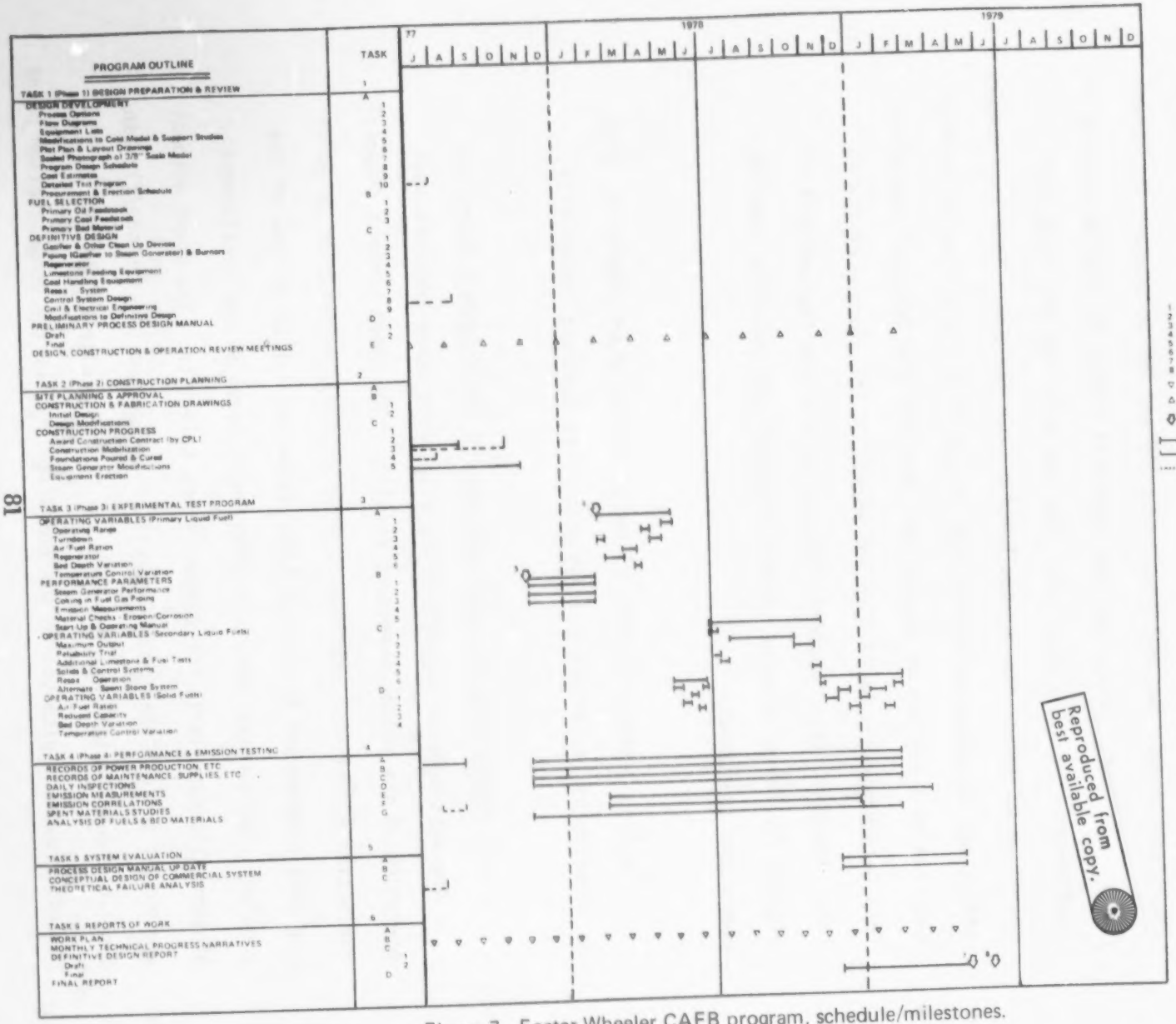

Figure 7. Foster Wheeler CAFB program, schedule/milestones.

6.2.2 CAFB Development and Technical Support (Esso Petroleum)

Esso will complete run 11 with an around-the-clock run of 200-plus hours and conduct two additional runs (12 and 13) to support the demonstration effort. These last two runs will either be problem solving or confirmation runs, as required. The runs will use the "long-day" technique to derive the maximum benefit from the test. Some exploratory effort may be conducted during runs 12 and 13 if the situation permits. Each run will include an around-the-clock 200-plus hours of operation. Esso personnel will be on site and assist in the startup of the La Palma demonstration. Further training on the Esso England unit is planned for Foster Wheeler startup engineers and possibly some CPL operations personnel.

The Esso schedule (Figure 8) and milestone chart (Table 11) give an overview of the effort planned under this contract (68-02-2159).

6.2.3 Engineering Analyses and Support (Westinghouse Research)

The Westinghouse support effort will place heavy emphasis upon operation of the solids transport facility. The spent sorbent disposal/evaluation effort will continue to provide timely information to guide the CAFB program and to provide information for the EA portion of the program. The sorbent selection effort will focus on the development of generalized criteria for sorbent stone selection. The spent sorbent processing and utilization effort will focus on the exact stone/fly-ash/spent-bed combination expected from the La Palma site as applied to potential uses or disposal in the immediate area of the demonstration plant.

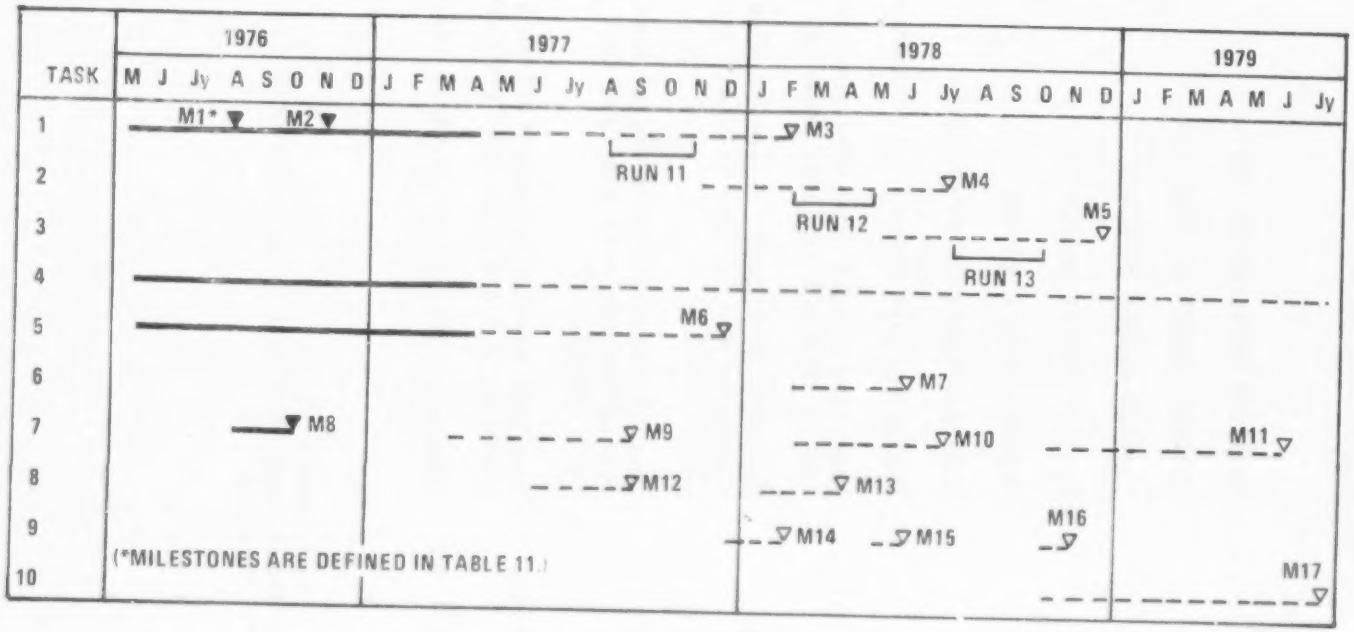

Figure 8. Esso Petroleum contract 68-02-2159, schedule.

TABLE 11. ESSO PETROLEUM CONTRACT

68-02-2159 PROGRAM MILESTONES

M1[a]	Complete mini-run on coal.
M2	Topical report on mini-run.
M3	Topical report on Run 11.
M4	Topical report on Run 12.
M5	Topical report on Run 13.
M6	Topical report on batch tests.
M7	Topical report on coal ash separation.
M8-M11	Incorporate data from mini-run, and Runs 11, 12, and 13 into mathematical model of process.
M12	Complete assistance to Foster Wheeler on operating procedure for oil and oil test program (Contract 68-02-2106).
M13	Complete assistance to Foster Wheeler on operating procedures for coal and coal test program (Contract 68-02-2106).
M14-M16	Complete visits to demonstration site to advise on startup, oil and coal test programs.
M17	Complete first draft of final report.

[a] Schedule complementing these milestones is shown in Figure 8.

Under the alternate concepts work area, Westinghouse will closely analyze the data developed at the demonstration unit to verify previous projections.

A number of alternative concepts for the CAFB process exist which have not been assessed in sufficient detail to draw conclusions as to their feasibility or performance. Experimentation, design, and cost and performance evaluations are required in the following suggested alternate areas in order to determine the proper direction for the demonstration plant program and CAFB commercial development:

- Sorbents.
- Fuels.
- CAFB applications.
- Processes (regenerative and once-through).
- Process arrangements.
- Plant component designs (solids transport systems).
- Plant layouts.
- Gasifier/boiler interface arrangements.
- Operating conditions.
- Operating procedures (turndown, startup, emergency).
- Control techniques.

Numerous alternatives to the base design exist which may improve the process economics and performance or may broaden its commercial applicability. Preliminary and conceptual assessments of these alternatives will be carried out with respect to the base design. Evaluations

will consider economic and environmental feasibility, problem areas, and development requirements.

Alternative concepts considered will include sorbents, fuels, applications, processes, designs, and operating concepts. Westinghouse will orient their activity to support more closely the demonstration effort. The Environmental Control Technology area will continue as before. As shown in the Figure 9 milestone chart, the multimedia emission and system evaluation will continue.

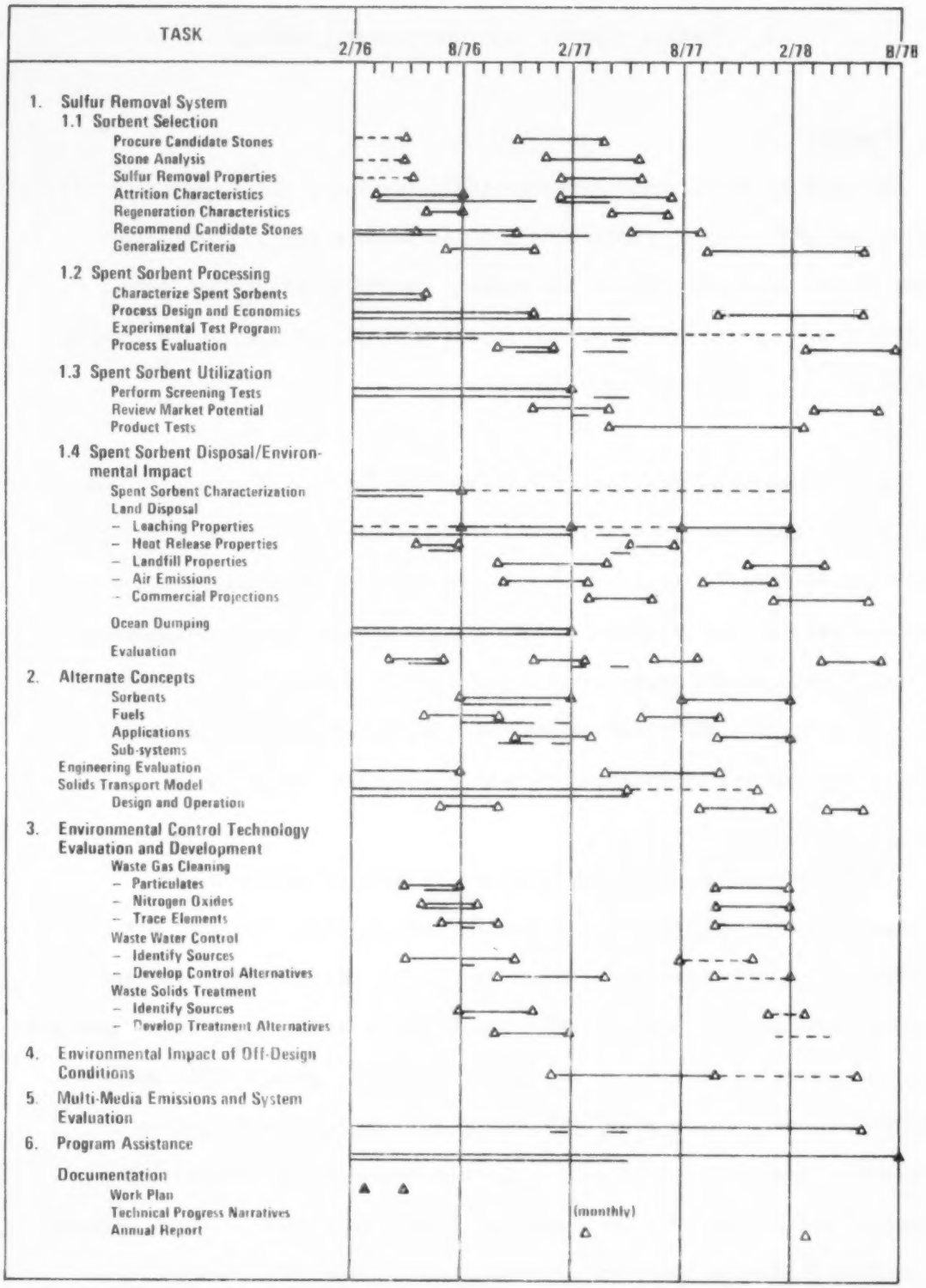

Figure 9. Westinghouse Research contract 68-02-2142, schedule/milestones.

7. CURRENT STATUS: HDS/HDN/DEMETALLIZATION

7.1 Progress

The work by Hydrocarbon Research (HRI) initially dealt with demetallization of residual oils. In a cooperative program between the U.S. and the Soviet Union, each side tested the other's demetallization catalyst on various residua to determine the relative merits of each. The results of this program are being evaluated.

As an offshoot of the demetallization project, an investigation was begun to evaluate the characteristics of available HDN catalysts using techniques that were similar to those used in the demetallization work. These evaluations are underway. The results of this phase are expected to provide data on the types of characteristics, such as active metal pairs and pore size distribution that would be most desirable in a catalyst for removal of nitrogen from high nitrogen liquid fuels.

The MIT work began with low pressure HDS/HDN of pyridene and thiophene. As mechanisms and theories were postulated, the work was expanded to include other model compounds (e.g., multi-ring sulfur and nitrogen compounds), higher pressure operation in order to be more representative of commercial operation, and better instrumentation. This work is providing information which will contribute to our understanding of the complex interactions; it will also help define better methods of removal of sulfur and nitrogen compounds from liquid fuels. These methods may involve different operating regimes, process sequence changes, or changes in catalysts.

Figures 10-12 show equipment being used for the HDS/HDN/Demetallization work.

7.2 Future Plans

The HRI program terminated in February 1978, and the MIT work will end in July 1978.

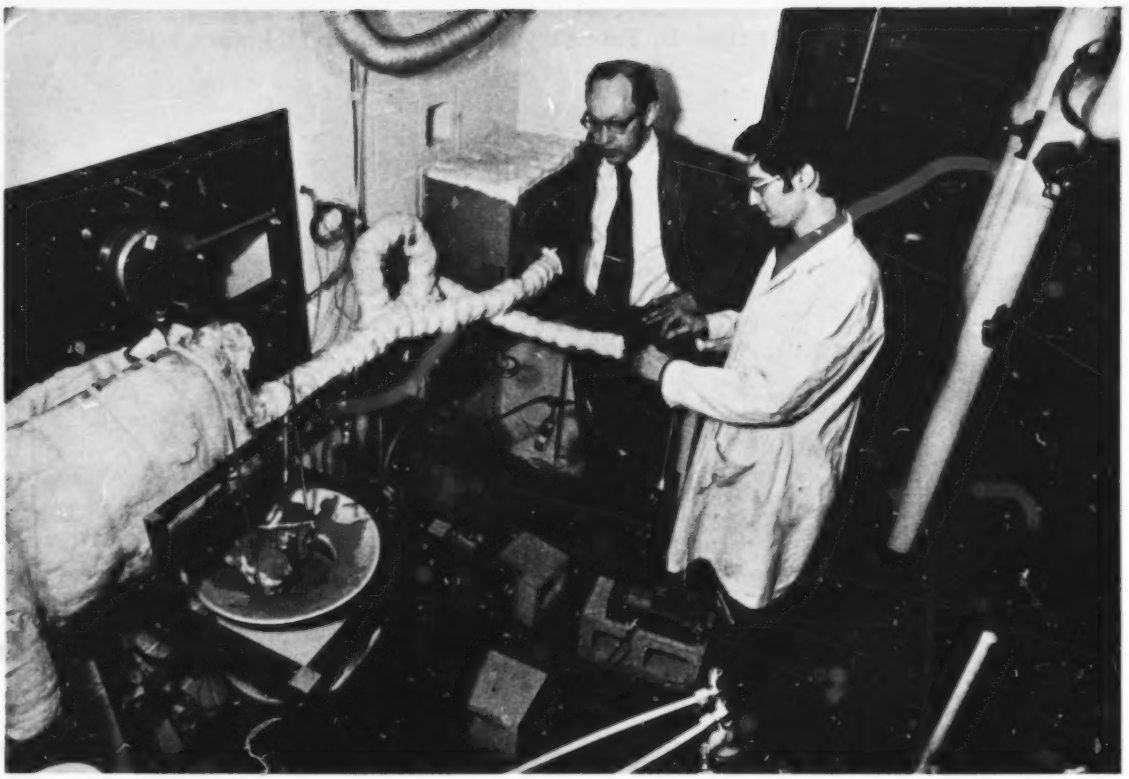

Figure 10. MIT Catalytic HDN/HDS facility--continuous microreactor featuring temperature control by a fluidized sand bath.

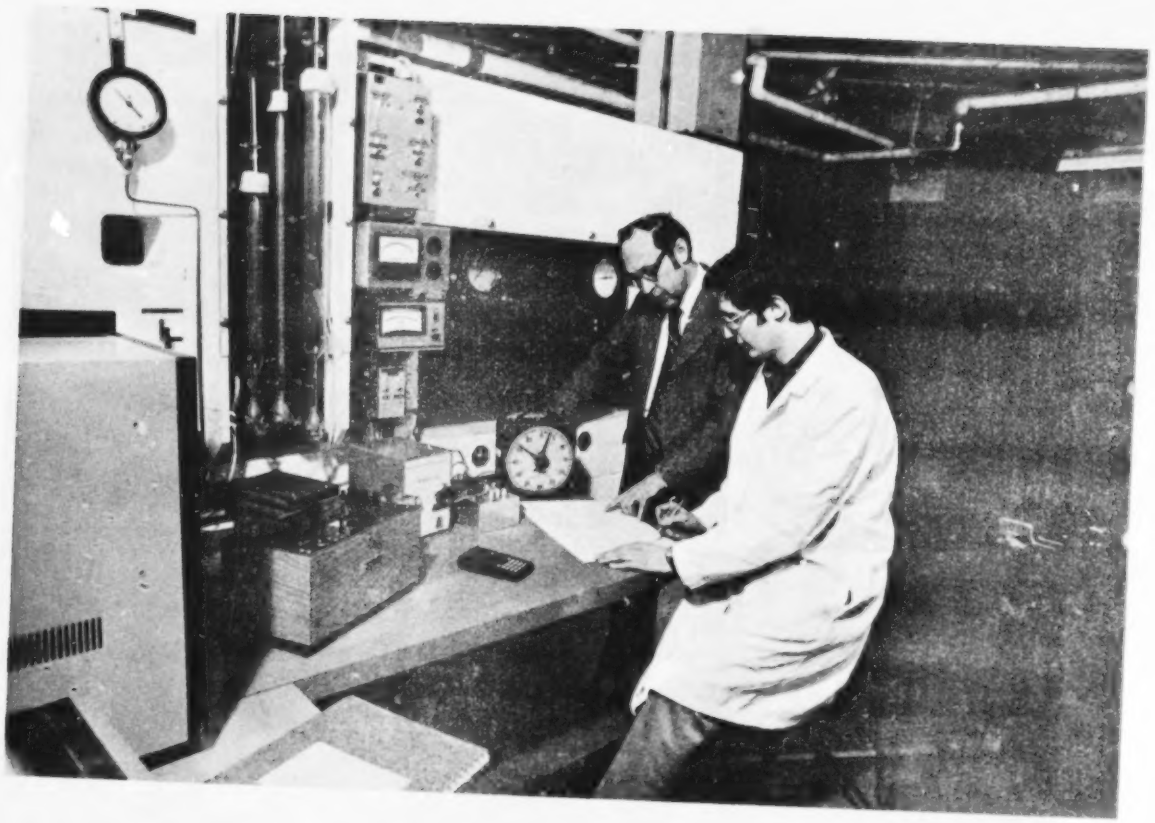

Figure 11. MIT Catalytic HDN/HDS facility--continuous microreactor instrumentation for high-pressure, low-flow operation.

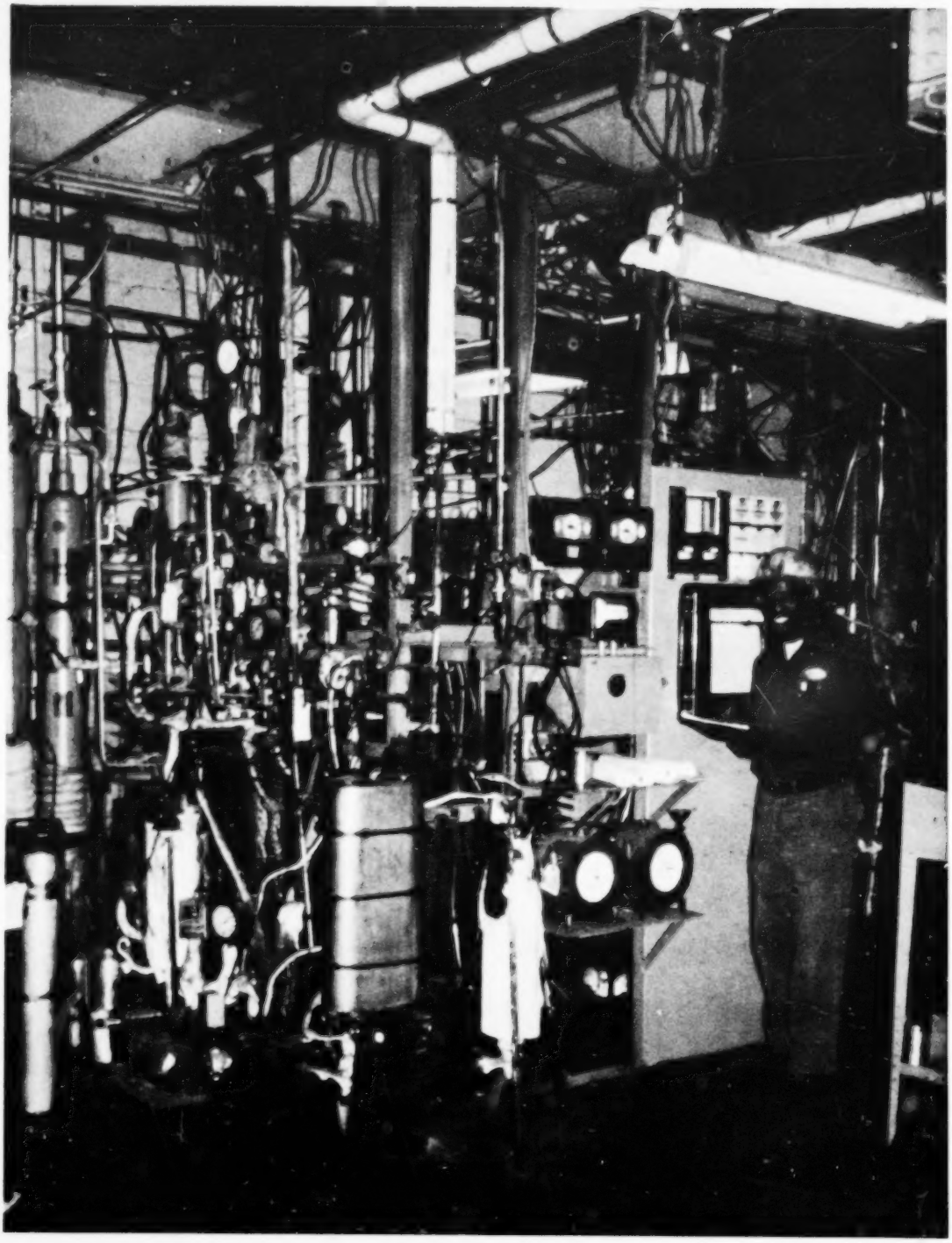

Figure 12. Hydrocarbon Research bench-scale demetallization unit.

8. APPENDICES

8.1 References

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